Estimation of Ni^{+2}

COMPLEXOMETRICALLY AND GRAVIMETRICALLY

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Complexometric Titrations

❖ It is a form of volumetric analysis, based on chemical characteristics of complexes and complex forming reactions to estimate relative proportions of metal ions in a sample

❖ Appearance or disappearance of coloured complexes dictates the end point

❖ EDTA is most widely used as complexone
   • Forms highly stable 1:1 complexes due to hexadenticity and chelation
   • Used as disodium salt (Na_2H_2Y), other forms are either acidic, basic or insoluble in water

❖ Ni^{+2} ions in a solution can be estimated by direct titration against EDTA, using Murexide (or Bromopyrogallol red) as metal ion indicator

❖ EBT cannot be used as $K_{f(Ni-EBT)} > K_{f(Ni-EDTA)}$ (Ni^{+2} is said to block the EBT indicator)

Murexide
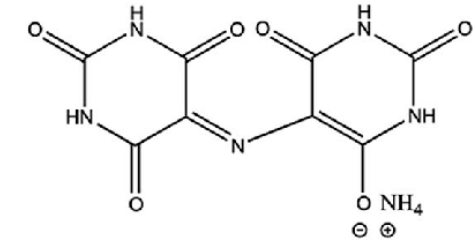
❖ It is one of the first metal ion indicators, and is ammonium salt of unstable purpuric acid. It has 4 protons (1 on each imido group) -> H_4D^-. Only 2 H can be deprotonated by an alkali hydroxide

pH

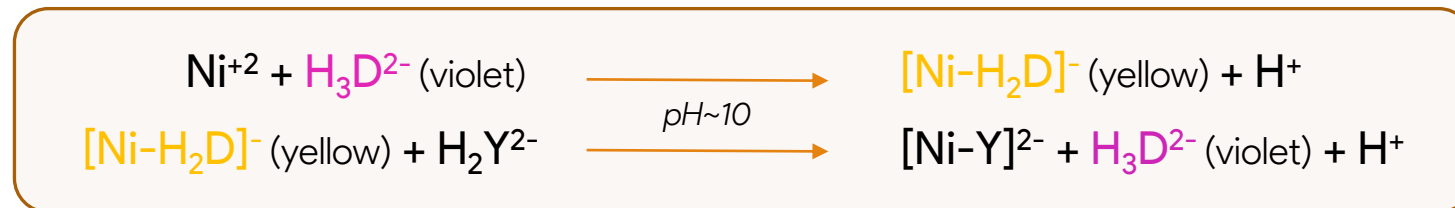9 ——————— 11

H_4D^- H_3D^{2-} H_2D^{3-}
(red-violet) pK_a 9.2   (violet) pK_a 10.5   (blue-violet)
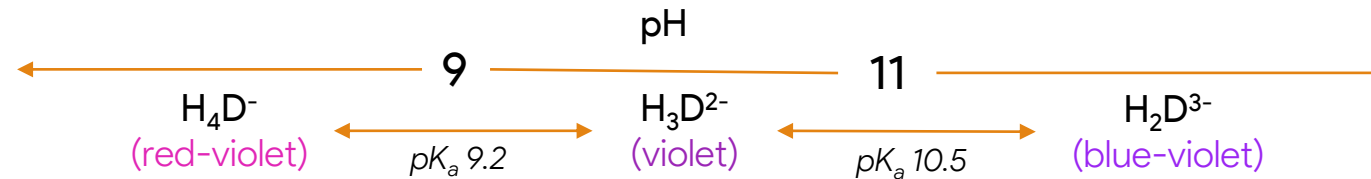
❖ Characteristics
  - Chromophores -> Carbonyl (C=O) and Imine (C=N-), Auxochrome -> Imido (batho and hyper chromic shifts)
  - Tridentate ligand (2 N and 1 O^-)
  - Both pH and pM sensitive. Hence, pH needs to be maintained using a buffer
  - pH range -> 9-11 (violet or blue-violet in free state)
  - Buffer -> NH_4OH-NH_4Cl (basic ammonical buffer)
  - Complexes -> Orange (Cu^{+2}), Yellow (Co^{+2}, Ni^{+2}), Red (Ca^{+2})

❖ Can be used in direct EDTA titration of Ni^{+2} at pH 9-11, end point yellow -> violet

❖ It has low affinity towards most metal ions, hence used in excess

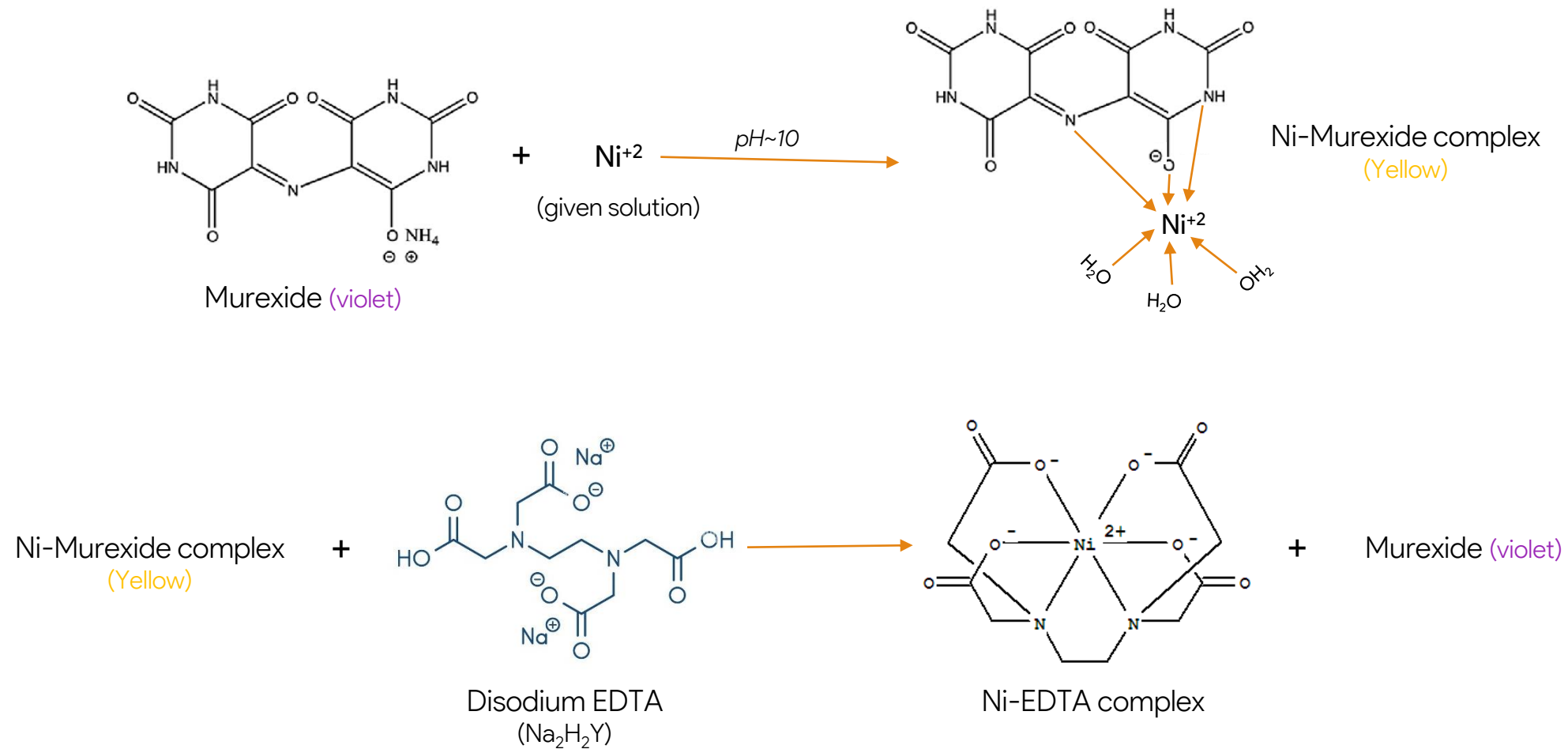❖ Aqueous solution of murexide are unstable and must be prepared each day
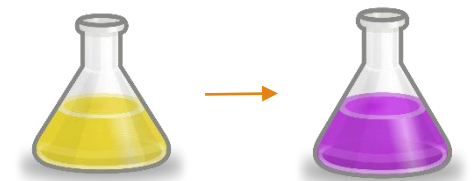
Principle

❖ Principle behind complexometric estimation of Ni^{+2} is that it forms stable complex with EDTA, which is more stable then it's complex with indicator (here murexide) ($K_{f(Ni-EDTA)} > K_{f(Ni-In)}$)

❖ If to an unknown sample of M^{+n}, suitable buffer (to maintain pH) and metal-ion indicator were added, indicator being a ligand forms complex with metal ions imparting colour to the solution (stability and colour depends on M^{+n} and pH)

❖ It can then be titrated against standard EDTA, which forms $[M-EDTA]^{n-4}$ complex owing to it's high stability. Near end point, EDTA progressively displaces M^{n+} ions from [M-In] complex

❖ At the end point, all of the M^{n+} ions were complexed by EDTA, leaving free indicator in the solution which causes a colour change

$$Ni^{+2} + H_3D^{2-} \text{ (violet)} \xrightarrow{\hspace{2cm}} [Ni-H_2D]^- \text{ (yellow)} + H^+$$

$$[Ni-H_2D]^- \text{ (yellow)} + H_2Y^{2-} \xrightarrow{pH\sim10} [Ni-Y]^{2-} + H_3D^{2-} \text{ (violet)} + H^+$$

❖ H^+ ions produced are neutralized by buffer

Murexide (violet)

+ Ni^{+2} $\xrightarrow{\text{pH~10}}$ Ni-Murexide complex (Yellow)

(given solution)

Ni-Murexide complex (Yellow) + Disodium EDTA (Na$_2$H$_2$Y) $\longrightarrow$ Ni-EDTA complex + Murexide (violet)

4. Complexometric Reactions

Requirements

❖ Chemicals Required

- Standard -> ZnO as primary standard
- Complexone -> Disodium EDTA
- Buffer -> NH_4Cl + NH_4OH solution (ammonical buffer)
- Indicators -> EBT and Murexide

❖ Apparatus Required

- Conical flasks and beakers
- Volumetric flask and measuring cylinder
- Test tubes
- Pipette
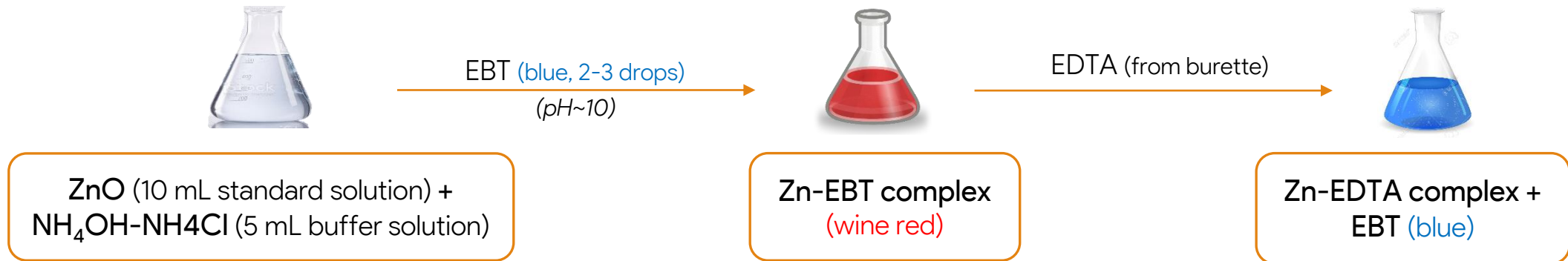- Burette
- Burette stand and white tile

Procedure

1. Preparation of standard ZnO solution (100 mL)

> **Calculated amount of ZnO** (s) **+ Few drops of HCl** (to completely dissolve ZnO in water) **+ Distilled water** (up to 100 mL mark) **--> Mixture was shaken well to get homogenous solution**
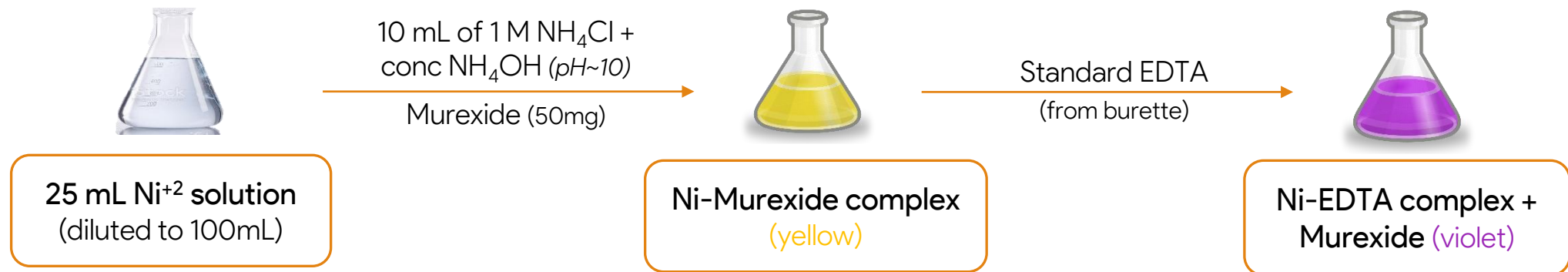>
> $$ZnO \text{ (s)} + 2HCl \text{ (aq)} \longrightarrow ZnCl_2 \text{ (aq)} + H_2O \text{ (l)}$$

2. Standardization of EDTA solution

EBT (blue, 2-3 drops)
(pH~10)

EDTA (from burette)

ZnO (10 mL standard solution) + **NH$_4$OH-NH4Cl** (5 mL buffer solution)

Zn-EBT complex
(wine red)

Zn-EDTA complex +
EBT (blue)

3. Estimation of Ni^{+2}

- Indicator -> 0.1 g murexide + 10 g KNO_3, grind well and use 50 mg of mixture in each titration
- Pipette 25 mL of given Ni^{+2} solution in a conical flask and dilute to 100 mL (with deionised water)
- Add 10 mL of 1 M NH_4Cl + conc NH_4OH buffer followed by 50 mg of indicator mixture
- If solution turns orange, add more conc NH_4OH until solution turns clear yellow (pH~10)
- Titrate against standard EDTA solution dropwise, until colour of solution changes from yellow -> violet at the end point (If at any intermediate stage, solution becomes orange, conc NH_4OH must be added to make it clear yellow)
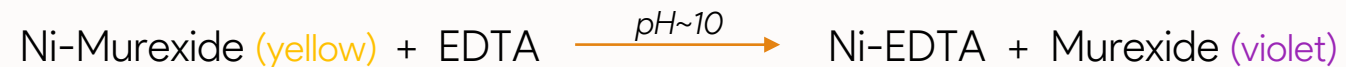- Ni^{+2} complexes slowly with EDTA, hence it must be added dropwise near the end point

10 mL of 1 M NH_4Cl +
conc NH_4OH *(pH~10)*

Murexide (50mg)

Standard EDTA
(from burette)

25 mL Ni^{+2} solution
(diluted to 100mL)

Ni-Murexide complex
(yellow)

Ni-EDTA complex +
Murexide (violet)

Calculations

Let normality of standard ZnO solution prepared be N_{ZnO}, then

❖ Normality of given EDTA solution

> Zn-EBT (wine red) + EDTA $\xrightarrow{\text{pH~9}}$ Zn-EDTA + EBT (blue)

- $N_{EDTA} \times V_{EDTA} = N_{ZnO} \times V_{ZnO}$ (V_{ZnO} = 10 mL)
- $N_{EDTA} = N_{ZnO} \times (10 / V_{EDTA})$ (V_{EDTA} obtained form step 2)

❖ Normality of Ni^{+2} in given solution

> Ni-Murexide (yellow) + EDTA $\xrightarrow{\text{pH~10}}$ Ni-EDTA + Murexide (violet)

- $N_{Ni+2} \times V_{Ni+2} = N_{EDTA} \times V_{EDTA}$ (V_{Ni+2} = 25 mL)
- $N_{Ni+2} = N_{EDTA} \times (V_{EDTA} / 25)$ (V_{EDTA} obtained form step 3)

Gravimetry

❖ It's a form of quantitative analysis by weight, and involves isolation and weighing of specie being determined (or compound of that specie)

❖ Principle -> If an element or radical under estimation forms a pure and stable compound with definite composition that can be readily isolated and weighed, then the amount of that element or radical in the test sample can be calculated just by relative atomic masses of constituent elements

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                        Isolation Methods
        ┌──────────────┬────────┴────────┬──────────────┐
   Precipitation   Volatilisation (or  Electroanalytical   Extraction and
                     Evolution)                            Chromatography
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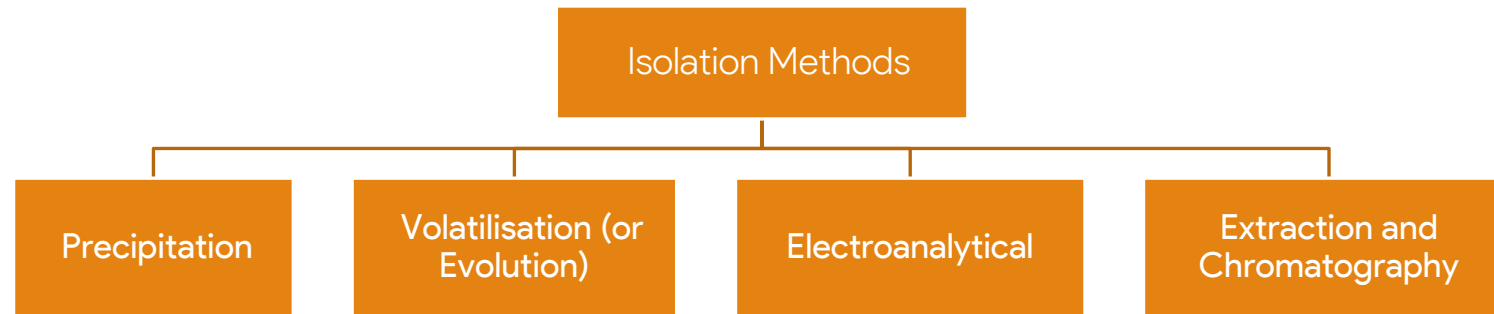
❖ Only significant disadvantage of this analysis technique is it's time consuming nature, which limits it's use in many places

Scope

❖ Advantages
- Absolute method, involving only direct measurements without any form of calibration
- Highly accurate and precise, with modern weighing balances
- Regular checking of possible error sources
  - Filtrate -> can be checked for completeness of precipitation
  - Precipitate -> can be checked for impurities
- **Mostly uses inexpensive apparatus** (the most costly being muffle furnace and platinum crucible in rare cases)

❖ Applications
- Analysis of standards for testing and calibration of instrumental techniques
- Analysis which require high accuracy
- Estimation of chemical composition, purity and thermal stability of compounds

Precipitation

It is the most widely used isolation method in gravimetric analysis. The element (or radical) under analysis is transformed into a insoluble precipitate, which can then be isolated

IDEAL PRECIPITATE

❖ It should be readily convertible to a pure compound with definite chemical composition, via simple chemical processes like
  - Ignition
  - evaporation with a suitable liquid, etc

❖ It should be highly insoluble, which on practical grounds means that
  - Very low K_{sp} (<< Ionic Product)
  - Amount of it left in solution should be less than least count of weighing balance used

❖ Physical nature should be such that it can be
  - **Readily separable by filtration** (large particle size)
  - **Washed free off soluble impurities** (particle size unaffected or at least not diminished by washing)

Precipitate Contamination

It's not necessary that precipitate that separates out of solution is always pure. Type and degree of contamination depends upon it's nature and condition of precipitation

Co-Precipitation

Contamination of ppt by substances which are normally soluble in mother liquor (co -> together)

- ❖ Surface Adsorption
  - Adsorption of contaminants over surface of ppt particles exposed to solution
  - Greatest for gelatinous (large surface area) ppt, minimum for macro-crystalline (large particle size) ppt
- ❖ Internal Contamination
  - Mostly occurs during fast building of precipitate from primary particles (coalescence)
  - Occlusion -> physical entrapment of contaminants adsorbed over primary particles (during fast coalescence) within ppt
  - Inclusion -> same as occlusion, but contaminants now occupies lattice sites within the ppt

Post-Precipitation

- Precipitation that occurs over the surface of main precipitate *after (or post)* it's formation
- Increases with time main ppt is left in contact with mother liquor
- Ex $Mg(C_2O_4)$ post precipitates over $Ca(C_2O_4)$ ppt

Digestion

Digestion is carried out by allowing ppt to stand for 12-24 hours or warming ppt for some time in contact with mother liquor

PURPOSE
- reduce contamination
- increase particle size and complete precipitation

EFFECT
❖ Small particles
- have high solubility and tend to pass in solution and re-deposit over larger particles
- Co-precipitation over minute particles is hence eliminated

❖ Rapidly formed crystals
- have irregular shape and high surface area, which on digestion becomes regular and dense
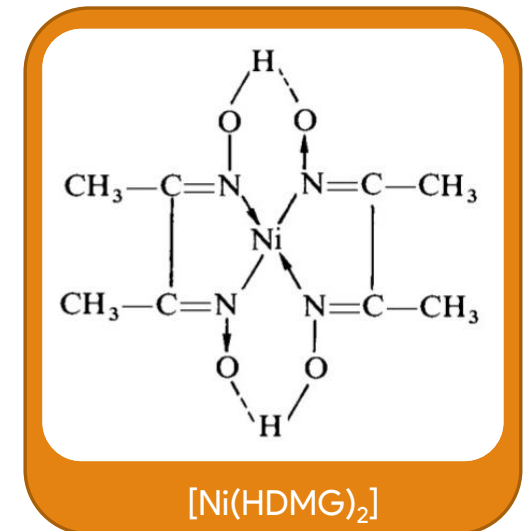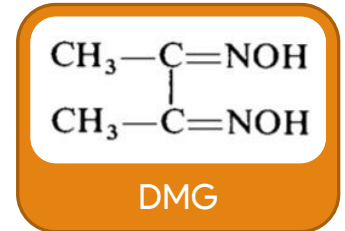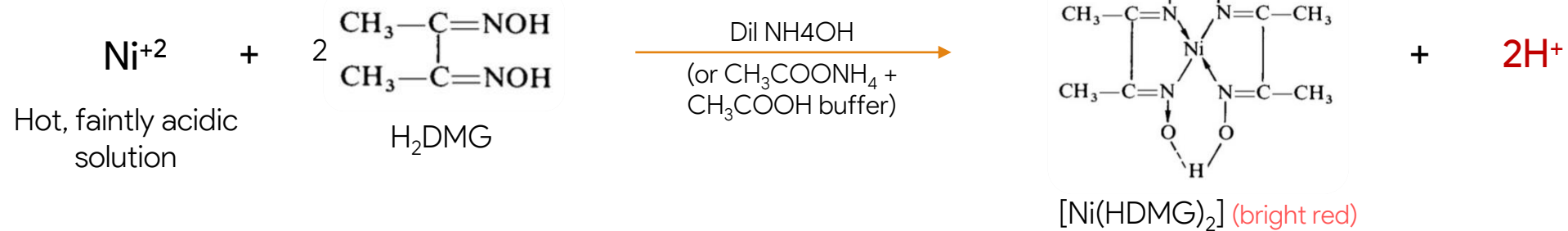- Result is decrease in surface area and adsorption

RESULT
- Decrease in overall co-precipitation
- Increase in particle size and ease of filtration
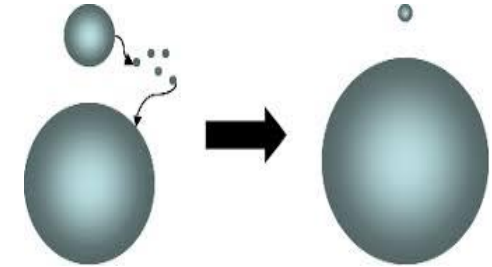
DMG

❖ Dimethylglyoxime $\{H_3C \cdot C(:NOH) \cdot C(:NOH) \cdot CH_3\}$ was discovered by L.Tschugaeff, and applied by O.Brunck in estimation of Ni^{+2} in steel

❖ Has 2 ionisable H -> H_2DMG

❖ Very slightly soluble in water (0.40g/L) -> used as 1% solution in 90% ethanol (rectified spirit) or absolute ethanol

❖ Can be used as disodium salt ($Na_2C_4H_6O_2N_2.8H_2O$), which is soluble in water

❖ Bidentate ligand, and forms a bright red $[Ni(HDMG)_2]$ complex with Ni^{+2}

❖ Large excess of DMG should be avoided because
  • It can itself precipitate due to low solubility in water
  • $[Ni(HDMG)_2]$ ppt can dissolve in high ethanol content (over 50%)

❖ Interference from Fe^{+3}, Al^{+3}, Cr^{+3} and Bi^{+2} is prevented by adding soluble tartrate or citrate, with which they form soluble complexes

$$Ni^{+2} + 2H_2DMG \longrightarrow [Ni(HDMG)_2] \text{ (bright red)} + 2H^+$$

DMG

$[Ni(HDMG)_2]$

Ni^{+2} + 2 H_2DMG $\xrightarrow{\text{Dil NH4OH (or } CH_3COONH_4 + CH_3COOH \text{ buffer)}}$ $[Ni(HDMG)_2]$ (bright red) + 2H$^+$

Hot, faintly acidic solution

- ❖ Ni^{+2} **solution is made faintly acidic** (by dil HCl)**, to prevent it's hydrolysis** (as $Ni(OH)_2$ is very insoluble, Ksp~5.85E-16) **and heated** (70-80°C) **to increase complexation rate**

- ❖ $[Ni(HDMG)_2]$ ppt Is *soluble* in
  - Free mineral acid (even as low as produces by reaction)
  - Solutions having > 50% ethanol (by volume)
  - In concentrated ammonia

- ❖ Therefore...
  - Large excess of DMG containing ethanol is avoided
  - *slight* excess of dil NH4OH or ($CH_3COONH_4 + CH_3COOH$) buffer is added to neutralise free mineral acids
  - CH_3COONa in place of CH_3COONH_4 should be used in presence of Mn, Co and Zn

15. Precipitation Reaction

Requirements
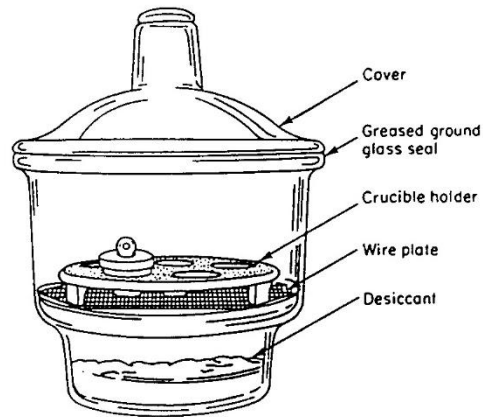
❖ Chemicals Required

- Ni^{+2} solution
- Dilute HCl solution (1:1)
- DMG reagent (1% solution in 90% or absolute ethanol)
- Dilute NH_4OH solution

❖ Apparatus Required

- **Crucible**
- **Desiccator** (sealable container with desiccants which absorb moisture from air, ex $CaCl_2$, $CaSO_4$. Used to sustain state of dryness)
- **Weighing balance**
- **Beakers (100 and 500mL)**
- **Test tubes**
- **Measuring cylinder**
- **Glass rod**

Cover
Greased ground glass seal
Crucible holder
Wire plate
Desiccant

DESICCATOR

BALANCE

CRUCIBLE

Procedure

❖ Preparation of NI^{+2} solution (200 mL)

> 0.3-0.4g (NH$_4$)$_2$SO$_4$.NiSO$_4$.6H$_2$O (Ammonium Nickel Sulphate) **in 500 mL beaker + 5 mL dil HCl** (1:1, to prevent hydrolysis) **+ dilute to 200 mL with distilled water**

❖ Precipitation of [Ni(HDMG)$_2$]

- **Heat Ni^{+2} solution to 70-80°C, and add slight excess of DMG reagent** (at least 5 mL for every 10 mg Ni^{+2})
- **Immediately add dil NH$_4$OH solution dropwise** (directly to solution rather down the sides of beaker) **with continuous stirring until precipitation occurs, and finally in slight excess**
- **Allow to stand on steam bath for 20-30 minutes, and then check for complete precipitation**
- **Allow ppt to stand for an hour, cooling at the same time**
- **Filter cold solution through a porcelain filtering crucible** (preheated to 110-120°C)
- **Cool the** Nickel Dimethylglyoximate (bright red) **precipitate in desiccator**

Drying and Weighing

- Wash [Ni(HDMG)$_2$] ppt with cold water (until free from soluble salts like chlorides)

- Dry at 110-120°C (or 150°C for high accuracy) for 45-50 minutes. This volatises any reagent that may have carried down with ppt

- Cool in desiccator (moisture free environment) and weigh

- Repeat the drying until constant weight is achieved

WET

DRIED

[Ni(HDMG)$_2$] PPT

Calculations

❖ **% of Ni in [Ni(HDMG)$_2$]**

- Molecular Formula -> $Ni(C_4H_7O_2N_2)_2$
- Relative atomic masses of constituents (u) -> Ni = 58.69, C = 12, H = 1, O = 16, N = 14
- Total Molecular Mass (u) -> 288.69
- % of Ni -> (58.69u / 288.69u) * 100 = 20.32%

❖ **Mass of Ni^{+2} in test sample (M_{Ni+2})**

Let mass of [Ni(HDMG)$_2$] measured experimentally (constant value) -> M_{Ni-DMG}

- Then, M_{Ni+2} = Mass of Ni^{+2} in [Ni(HDMG)$_2$]
- M_{Ni+2} = (% of Ni in complex / 100) * M_{Ni-DMG}
- M_{Ni+2} = (20.32 / 100) * M_{Ni-DMG}
- M_{Ni+2} = 0.2032 * M_{Ni-DMG}

Comparison

Complexometry	Gravimetry
Reasonably accurate (depends upon stability of M-In and M-EDTA complex)	Highly accurate (depends upon nature of specie being isolated)
Quick estimation	Consumes lot of time
Relative method (involves titration against standards)	Absolute method (no calibration required)
Highly error prone (pH sensitivity, low stability of complexes, indicator error etc)	Error sources (filtrate and precipitate) can be easily checked
Can produce a lot of waste	Waste is mostly limited to reagents and isolated compound
Used to estimate relative proportions of metal ions in the solution	Used in high accuracy demanding areas, like analysis of standards

References

- ❖ Vogel's textbook of quantitative chemical analysis
- ❖ https://en.wikipedia.org
- ❖ https://chemistry.stackexchange.com
- ❖ https://www.chemeurope.com/en/encyclopedia