Estimation of Zn^{2+} & Pb^{2+} ions

IN A GIVEN SOLUTION COMPLEXOMETRICALLY

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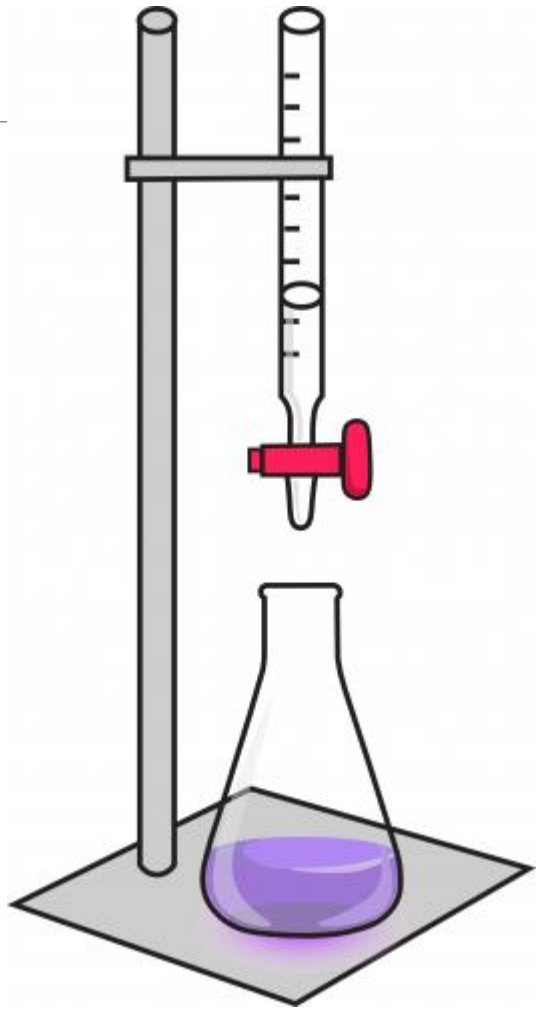
Chemicals Required

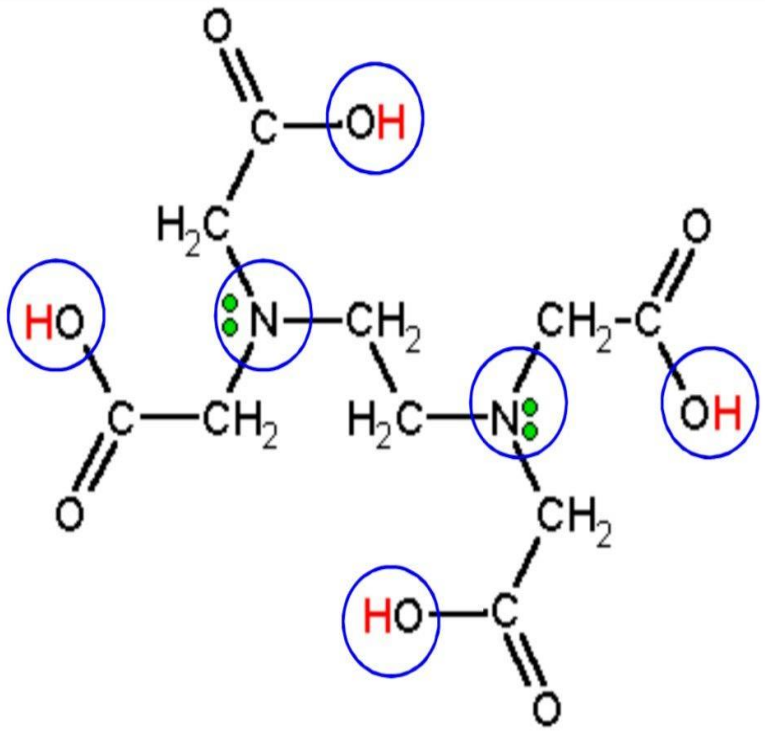
- Complexone: EDTA solution
- Standard: ZnO as primary standard
- Indicators: Eriochrome Black-T (EBT) and Xylenol Orange (XO)
- Buffers: NH_4OH-NH_4Cl solution and Hexamine
- Auxiliaries: Ammonium acetate and acetic acid

Complexometric Titrations

- Complexometric titrations are a form of volumetric analysis in which the formation of a colored complex is used to indicate the end point of a titration
- These are used mainly to determine metal ions in a mixture by use of complex-forming reactions
- Most common chelating agent used for in these titrations is EDTA



Why EDTA??



6 metal binding sites making it hexadentate ligand

- Reasons for using EDTA
  - Forms strong 1 : 1 complexes with most metal ions
  - Large formation constants with many metal ions
  - Forms stable, water-soluble metal complexes
- Titrations with EDTA gets affected by pH factor, stability constant of the complex formed etc.
- pH is important to guarantee the selectivity and accuracy of the analysis
- The more stable the chelate, the lower the pH at which the titration can be performed.

Estimation of Zn^{2+} & Pb^{2+}

IN A MIXTURE

- Zn^{2+} and Pb^{2+} when present simultaneously in a solution can be estimated using direct titration with EBT and Xylenol Orange indicator in different pH ranges
- Different pH range is preferred for increasing selectivity
- Before proceeding to titration, Zn^{2+} and Pb^{2+} ions must be separated using a suitable precipitating agent.
- Another technique that might also be used is *masking* which eliminates the need for separating both the ions
- Cyanide ion can be used as masking agent in this method.

Need for separation of Zn^{2+} and Pb^{2+}

Formation constant of metal-EDTA complex:

$$K_f = \frac{[M\text{-}EDTA]}{[M][EDTA]}$$

A metal, M can be very easily titrated in presence of other metal, N if the formation constant values of these ions is such that:

$K_M/K_N >= 10^8$ (in presence of complex forming indicator)

But

K_f (Zn-EDTA complex) = $10^{16.5}$
K_f (Pb-EDTA complex)= $10^{18.0}$

making $K_f(Pb)/K_f(Zn) = 10^{1.5}$

Because of this proximity of formation constant values of these two complexes, Zn^{2+} and Pb^{2+} must be separated before proceeding to titration. (formation of both Zn-EDTA and Pb-EDTA complexes in the same solution makes it difficult to estimate their concentrations individually)

Separation of Pb^{+2}

- Precipitating agent is chosen in such a way that it forms a precipitate with only one of the metal ion leaving out the other in the solution form
- Precipitating agent: K_2SO_4 solution. In case K_2SO_4 is unavailable, K_2SO_3 or Na_2SO_3 can be used after oxidation with HNO_3
- Conditions for precipitation:
  - ionic product > solubility product (K_{sp})
  - Size Compatibility between cation and anion
  - lattice energy > hydration energy

$PbSO_4$ satisfies all the 3 criteria

$K_{sp} = [Pb^{2+}] \times [SO_4^{2-}] = 2.53 \times 10^{-8}\ M^2$
Size of Pb^{2+} = 119 pm
Solubility = 0.00443 g/100 mL (20 °C)

- $Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$: much more stable, white ppt is obtained
- Water's dipole strength is too weak to pull away the ions (both anions and cations) from the strong crystals of lead sulphate
- Solution is warmed to increase rate of precipitation. K_2SO_4 is added dropwise to avoid super saturation
- $ZnSO_4$ if formed, is soluble in water

Digestion of precipitate

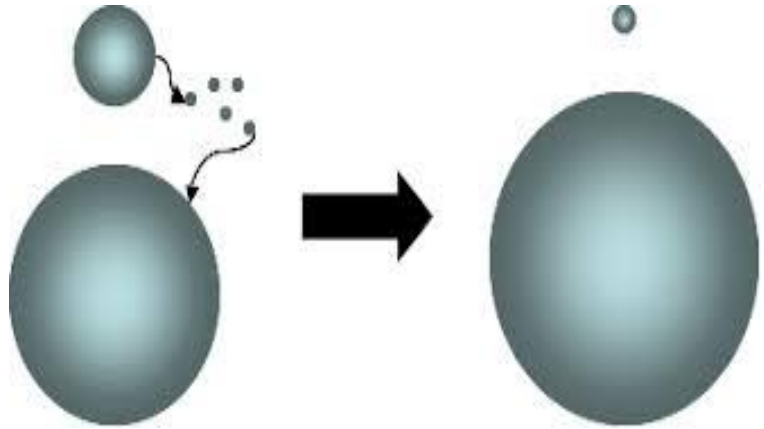
Occurs when a freshly-formed precipitate is left, usually at a higher temperature, in the solution from which it is precipitated.

Need: Results in bigger particles, generally purer, easier to wash & filter → Ostwald ripening

larger particles → greater volume to surface area ratio → lower energy state (more favored)

Molecules on the surface of a particle → energetically less stable than the ones already well ordered and packed in the interior.

System tries to lower its overall energy → molecules on the surface of a small particle tend to diffuse through solution and add to the surface of larger particle.



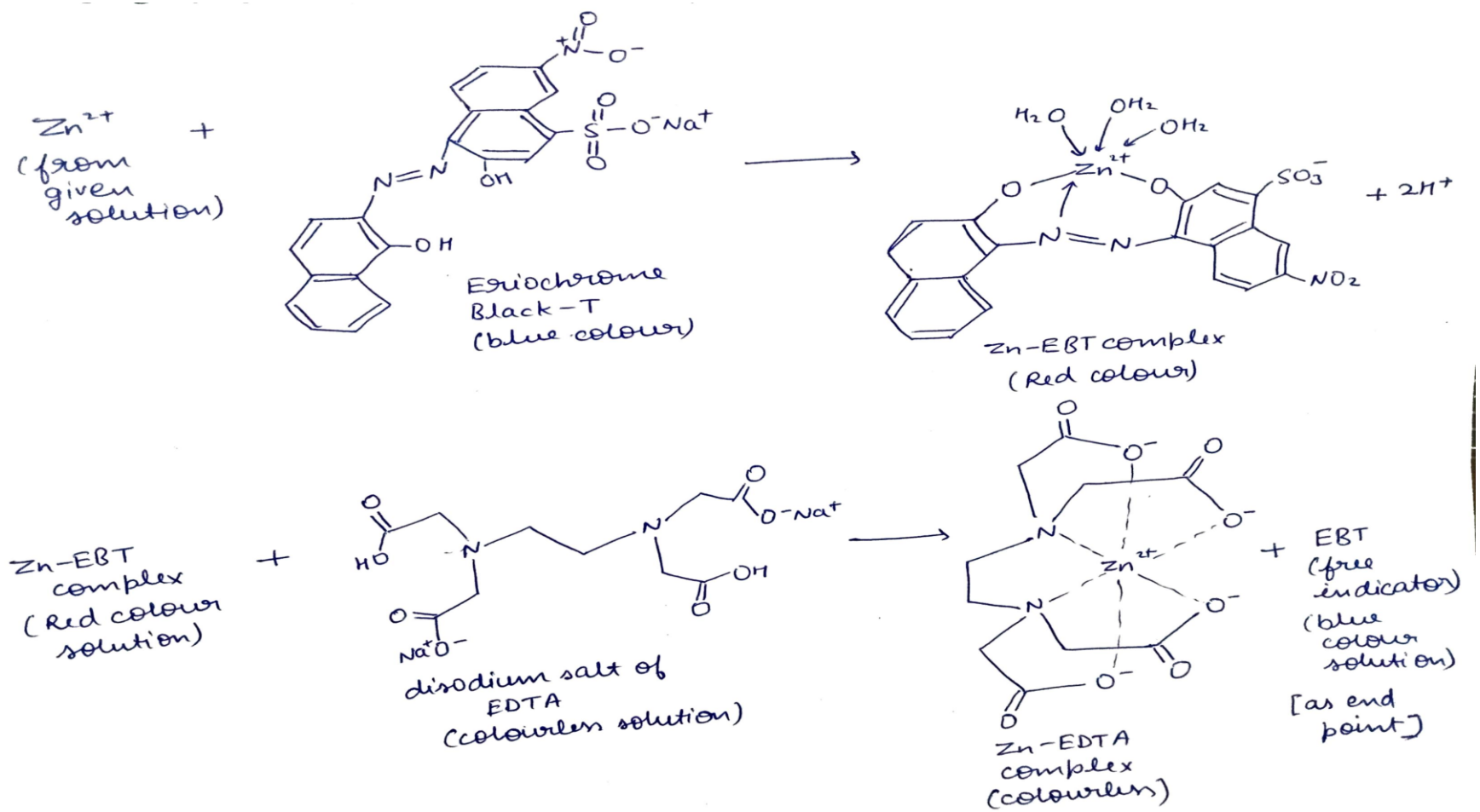
Energetic factors → large precipitates grow, drawing material from the smaller precipitates, which shrink

Estimation of Zn^{2+} ions

- Zn^{2+} ions in the solution are estimated by titrating the filtrate with EDTA solution using EBT as indicator.
- K_f (Zn-EBT) < K_f (Zn-EDTA) } Difference in number of ligating centres in EBT and EDTA

- pH range = 10 (NH_4OH-NH4Cl buffer is added)
  - For neutralizing effect of H+ ions released on reaction of Zn^{2+} with EDTA and EBT: Enables the formation of the Zn^{2+} with EDTA at the appropriate pH
  - avoid the Zn^{2+} ion precipitation (as $Zn(OH)_2$) in alkaline pH

$Zn2^{+}$ + EBT (blue) ➔ Zn-EBT (wine red colour) + 2H+
Zn-EBT (wine red) + EDTA ➔ Zn-EDTA + EBT (blue)



9. Reactions for estimation of Zn^{2+}

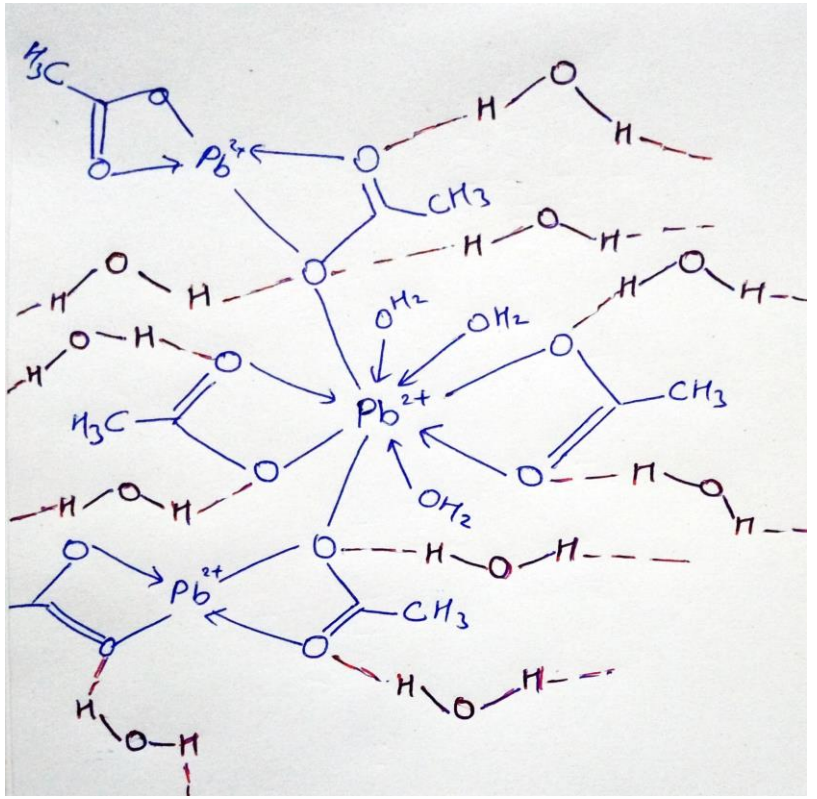
Dissolution of $PbSO_4$ ppt

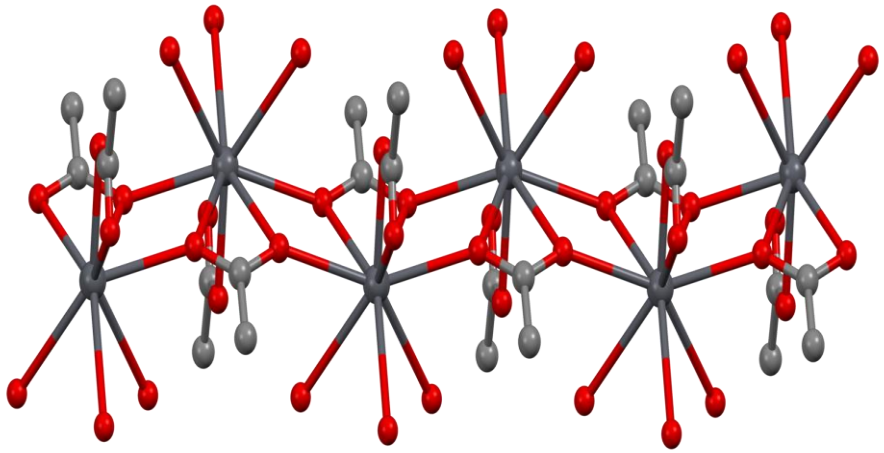
- Dissolved using ammonium acetate and acetic acid

$PbSO_4 + 2CH_3COONH_4 \rightarrow Pb(CH_3COO)_2 + (NH_4)_2SO_4$ (insoluble) (soluble)

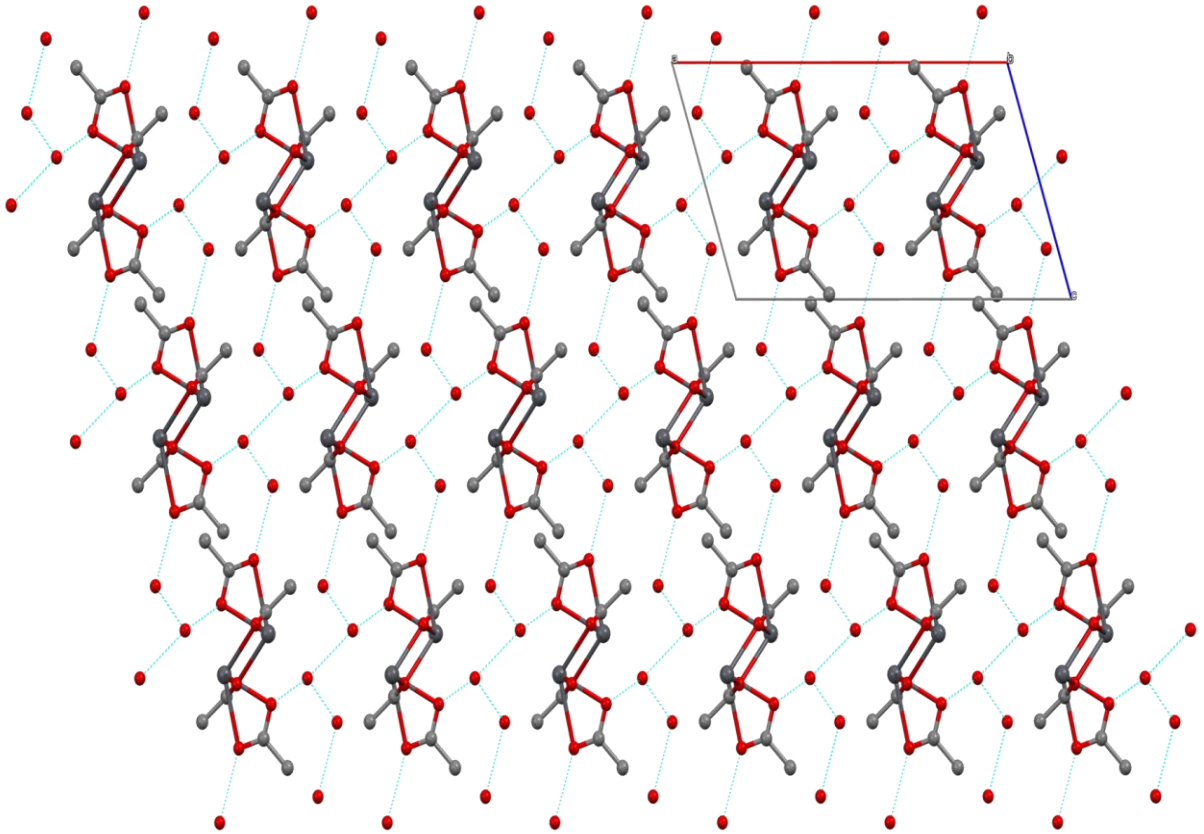
$Pb(CH_3COO)_2 + H_2O \rightarrow Pb(CH_3COO)_2.3H_2O$ (Soluble)

- Why lead acetate is soluble???
- It is soluble because of hydrogen bonding present due to its structure. In the trihydrate, the Pb^{2+} ion's coordination sphere consists of nine oxygen atoms belonging to 3 water molecules, two bidentate acetate groups and two bridging acetate groups.
- Uses: keeps Pb^{2+} in solution form preventing its hydrolysis





Hydrogen bonding in the crystal structure

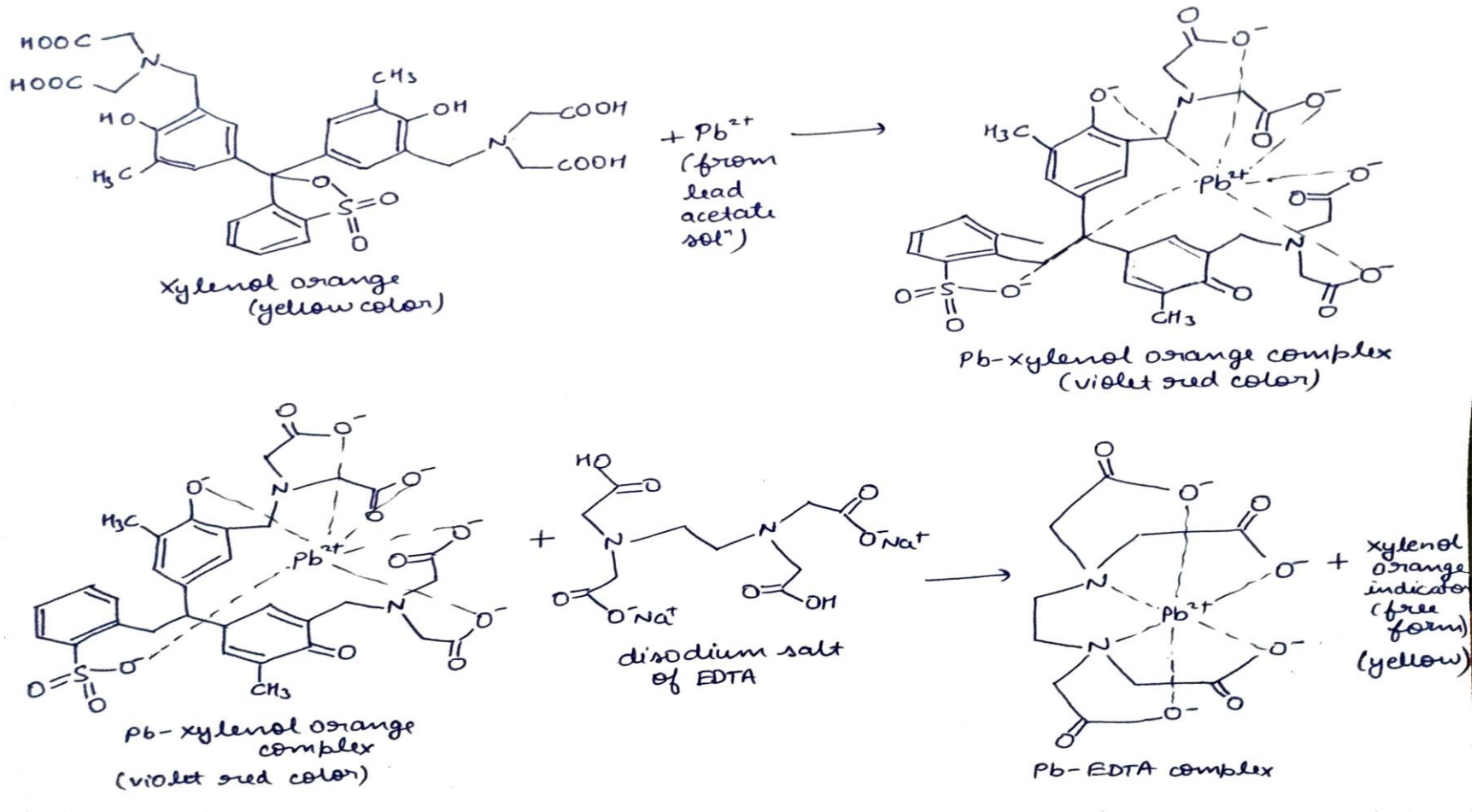


11. Structure of Lead Acetate (trihydrate)

Estimation of Pb^{2+} ions

- $Pb2^{+}$ ions in the solution can then be estimated by direct titration with EDTA solution using Xylenol Orange as indicator.
- pH maintained is 5 ➔ obtained by adding hexamine buffer solution
- Why 5-6 pH??
  - For maximum stability of Pb-EDTA complex
  - to increase selectivity of EDTA
  - To prevent hydrolysis of Pb^{2+} ions

Pb^{2+} + XO (lemon yellow) ➔ Pb-XO (violet red)
Pb-XO (violet red) + EDTA ➔ Pb-EDTA + XO (lemon yellow)



13. Reactions for estimation of Pb^{2+}

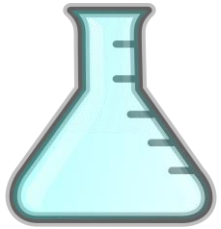
Procedure

1. Preparation of standard solution of ZnO in 100 mL

Calculated amount of ZnO + Few drops of HCl (to make ZnO completely dissolve in water) + Distilled water up to 100 mL mark ➔ Mixture is shaken well to get homogenous solution

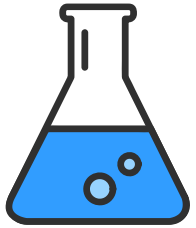
$$ZnO(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2O(l)$$

2. Standardization of EDTA solution with std ZnO sol: EDTA solution is taken in burette.



10 mL std ZnO sol + 5 mL of NH_4OH-NH4Cl buffer

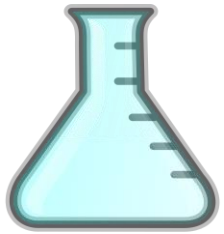
On adding a few drops EBT indicator, Zn-EBT complex (wine-red) is formed



At end point, EDTA replaces EBT from Zn-EBT complex giving blue colour

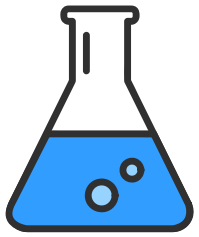
3. Separation of Pb^{2+} and Zn^{2+} solution
   - 20 mL of distilled water is added and heated up to 60 °C.
   - 10% K_2SO_4 solution is added dropwise until completion of precipitation
   - Solution is digested for about 10 min
   - A drop of K_2SO_4 was added to check for completion of precipitation
   - Solution is filtered using whatmann filter paper

4. Estimation of Zn^{2+} solution
   - Solution in burette: standardized EDTA



10 mL filtrate + 5 mL of NH_4OH-NH4Cl buffer

On adding a few drops EBT indicator, Zn-EBT complex (wine-red) is formed



At end point, EDTA replaces EBT from Zn-EBT complex giving blue colour

5. Estimation of Pb^{2+} in given solution
   - Precipitate of $PbSO_4$ is dissolved using CH_3COONH_4 & CH_3COOH
   - Solution is made up to mark of 100 mL
   - Solution in burette: standardized EDTA solution

10 mL of Pb^{2+} sol. + hexamine buffer

On adding a few drops of XO indicator, Pb-XO complex (violet-red) is formed

EDTA replaces XO from Pb-XO complex➔ free XO (lemon-yellow) is obtained

Calculations

Let normality of std ZnO solution prepared be N_{ZnO}.

- **Normality of given EDTA solution**: *Zn-EBT (wine red) + EDTA ➔ Zn-EDTA + EBT (blue)*
  - $N_{EDTA} \times V_{EDTA} = N_{ZnO} \times V_{ZnO}$
  - $N_{EDTA} = (N_{ZnO} \times 10) / V_{EDTA}$ (V_{EDTA} obtained form step 2)

- **Normality of Zn^{2+} in given solution**: *Zn-EBT (wine red) + EDTA ➔ Zn-EDTA + EBT (blue)*
  - $N_{EDTA} \times V_{EDTA} = N_{Zn2+} \times V_{Zn2+}$
  - $N_{Zn2+} = (N_{EDTA} \times V_{EDTA}) / 10$ (V_{EDTA} obtained form step 3)

- **Normality of Pb^{2+} in given solution**: *Pb-XO (violet red) + EDTA ➔ Pb-EDTA + XO (yellow)*
  - $N_{EDTA} \times V_{EDTA} = N_{Pb2+} \times V_{Pb2+}$
  - $N_{Pb2+} = (N_{EDTA} \times V_{EDTA}) / 10$ (V_{EDTA} obtained form step 4)

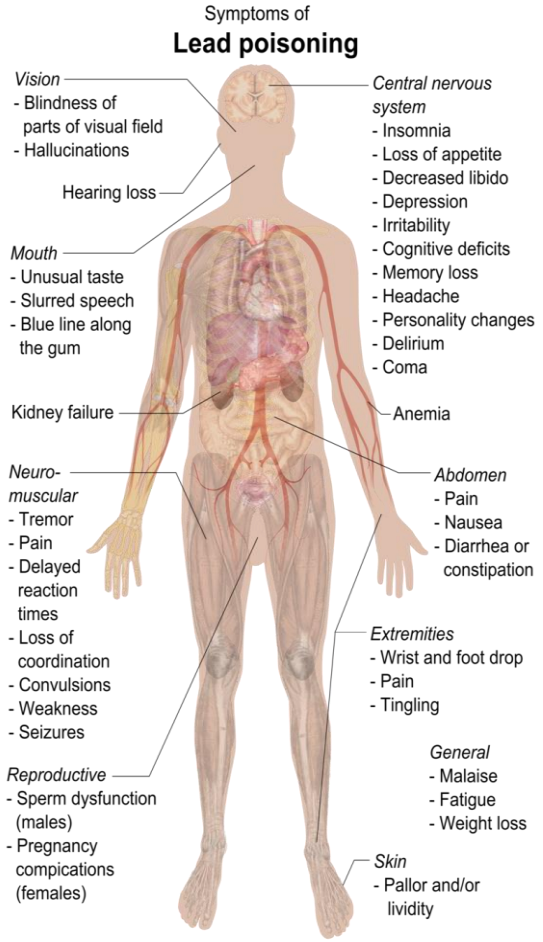
Applications

OF TODAY'S EXPERIMENT

- Analysis of various lead-containing alloys such as bronzes, ounce metal, solders and tin- and lead-based alloys
- Analysis of content in zinc-lead ore
- Analysis of glass certified reference material– optical glasses etc.
- Removal of zinc and lead contamination from water, sewage and soil by estimating them

Precautions

- Lead is a highly poisonous metal (whether inhaled or swallowed), affecting almost every organ and system in the human body. Hence masks and gloves are must while handling solution containing Pb^{2+} ions.
- Cu, Co, Ni, Cr, Fe, Al even in traces must be absent as they interfere in the titration by forming more stable M-EDTA complexes.
- Deionized water is preferred over distilled water.
- $PbSO_4$ ppt must be washed properly so as to make sure removal of Zn^{2+} solution from it.
- Burette must be rinsed with EDTA solution before titrations.



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