Semester: I

CHEMISTRY OF SMART MATERIALS AND DEVICES (22CHY12A)

(Category: Professional Core Course) Stream: CS (Theory and Practice)

Practical:
Expt-1: Estimation of Copper from PCBs e-waste

C. MANJUNATHA, Ph.D, MRSC
Assistant Professor, Department of Chemistry, RV College of Engineering
Bengaluru-560059, INDIA, Phone: +91 9036651277
E-mail: manjunathac@rvce.edu.in; manju.chem20@gmail.com

Estimation of Copper from PCBs e-waste

"E-waste", "electronic waste", "e-scrap" Are used electronics that are nearing the end of their useful life, and are discarded.

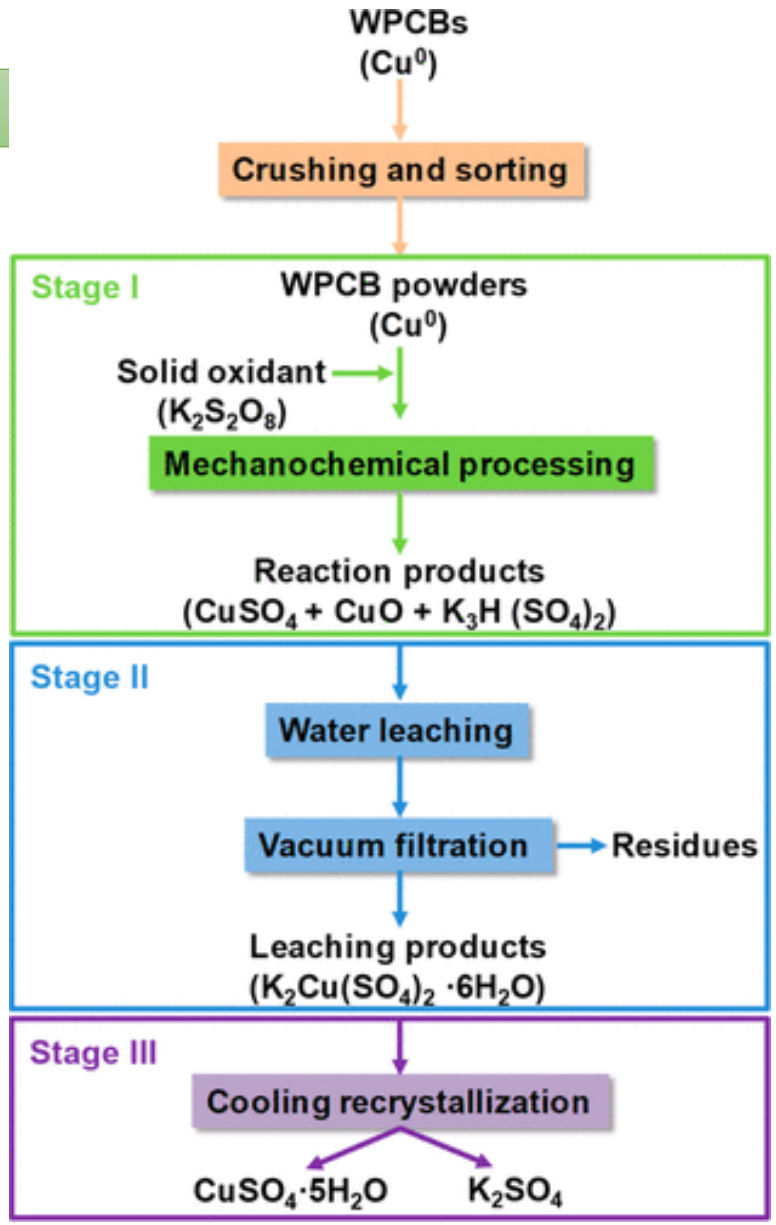
Waste printed circuit boards (PCBs)

- PCBs comprise metals (Cu, Sn, Pb, Ag, Au, Pd, Fe, Ni, and Cr), nonmetals (glass fibers, electronic component insulators, capacitors, resistors, and so on), and organic compounds (epoxy resin, paints...).
- Copper is the primary component of PCB, which is employed as an electric current conductor.
- These discarded metals without treatment threaten the economy, the environment, and human health.

https://cen.acs.org/articles/91/web/2013/07/Circuit-Board-Waste-Mops-Toxic.html

Estimation of Copper from PCBs e-waste (Waste PCBs: WPCB)

1. All the detachable components free from copper (e.g., relays, capacitors, and resistance) were separated, the bare PCB boards were shredded and crushed by a cutting and grinding machine and passed through a sieve mesh to obtain the WPCB powder of varying particle sizes.
2. Then the mixer of WPCB powder and $K_2S_2O_8$ (with suitable mass ratios) together with grinding balls, were sealed in the ZrO_2 pot. The mixture was then co-ground at different rotary speeds under ambient conditions for different periods of time **(Stage I).**
3. Co-ground products of PCB powder and $K_2S_2O_8$ is leached in deionized water with constant magnetic stirring at different temperatures: 25, 35, 45, and 55 °C. The leaching solution and solid residues were rapidly separated by vacuum filtration after the reaction was complete. **(Stage-II).**
4. After filtration, $CuSO_4 \cdot 5H_2O$ could be easily separated from K_2SO_4 solution because of their differences in solubility. **(Stage-III)**



The flowchart for Cu recovery from PCB powder is shown in Figure.

https://doi.org/10.1021/acs.est.8b06081

Estimation of Copper from PCBs e-waste (Waste PCBs: WPCB)

How Cu is estimated? **Iodometeric method.**

1. $2CuSO_4 + 4KI \longrightarrow 2CuI_2 + 2K_2SO_4$

2. $2CuI_2 \longrightarrow Cu_2I_2 + I_2$
(Unstable Cupric iodide) (Stable Cuprous iodide)

3. $2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$
(O. S. of S_2 : + 4) (O. S. of S_2 in sodium-tetrathionate : + 5)

Here $2Cu = I_2 = 2Na_2S_2O_3$

$[Cu] = [Na_2S_2O_3]$

❖The I_2 liberated is estimated using Std. $Na_2S_2O_3$ solution by **IODOMETRIC** titration method.

❖**The amount of $Na_2S_2O_3$ consumed is equivalent to [Cu] present in water.**

Estimation of Copper from PCBs e-waste

Model Procedure:

Step-1 : Extraction of copper from e-waste (PCBs

After removing all the detachable components, the PCB boards are crushed to powder is mixed with $K_2S_2O_8$ (Oxidant) and ball milled to fine powder. The fine mixer of PCB+ $K_2S_2O_8$ powder is leached in deionized water and nitric acid with constant stirring at 55 °C. The leached solution and solid residue is separated by filtration. After the filtration, the copper solution is mixed with nitric acid to prevent hydrolysis. (called PCB solution)

Step-2: Preparation of Standard Sodium Thiosulfate solution ($Na_2S_2O_3$)

The accurate quantity ('w' g) of $Na_2S_2O_3.5H_2O$ (Molecular Weight =Equivalent wt=248.18) is weighed and dissolved in 100 ml of pure distilled water in 100 ml volumetric flask.

Normality of $Na_2S_2O_3.5H_2O$ = (w x10)/Equivalent wt = 'Y' N

Step-3 Titration

Burette: Standard ('X'N) $Na_2S_2O_3$ solution

Conical flask: 25 ml of PCB solution + 1 spatula urea + Heat near to boil + cool to room temperature + Ammonium hydroxide drop by drop till to get bluish with precipitate + ¼ test tube acetic Acid (~5 ml) + 1 test tube of KI (~15 ml) …….(dark brownish yellow solution with white precipitate appears) + titrate against $Na_2S_2O_3$ solution till to get pale yellow color + add 5 drops of starch indicator+ solution turns blue+ continue titration till to get permanent pure white solution. (End point Reached)

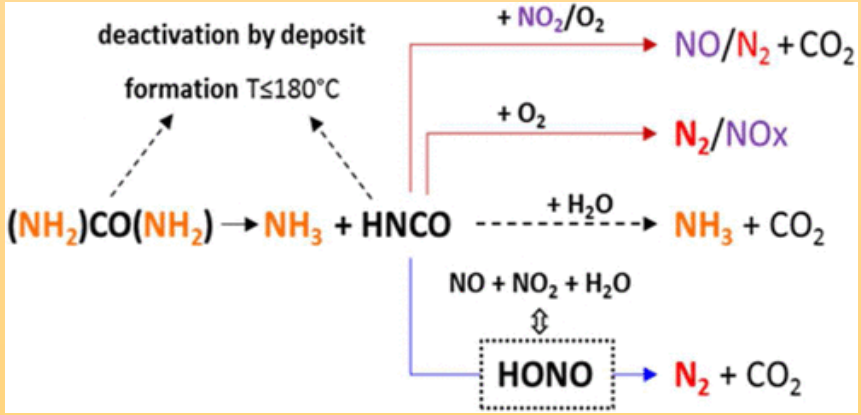
Note down the volume of 'V' ml for estimation of copper in PCB solution.

1000 ml of PCB solution contains= {Vx Y x 63.54} / 25 g

Estimation of Copper from PCBs e-waste (Waste PCBs: WPCB)

Role of chemicals added

Urea :
It removes nitrogen oxides



Ammonium hydroxide :
It neutralises the excess H^+ ions (Acidic to basic)

$NH_4OH + H+ \rightarrow NH_4^+ + H_2O$ (drop by drop)

$NH_4OH + Cu^{2+} \rightarrow Cu(OH)_2$ blue ppt + NH_4^+

Acetic acid:
It neutralises the $Cu(OH)_2$ and provides the required slightly acidic medium of pH =3-4.

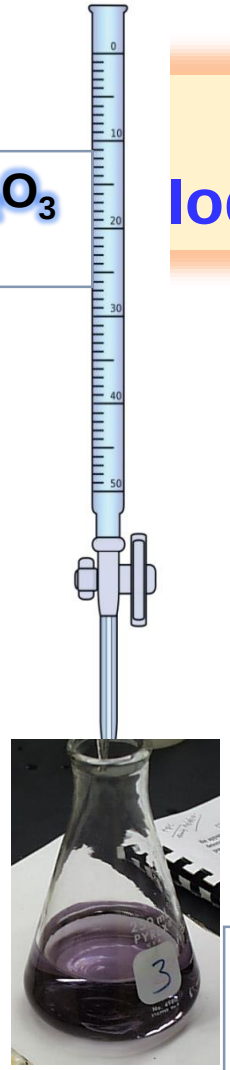
$Cu(OH)_2 + CH_3COOH \rightarrow Cu(CH_3COO)_2 + H_2O$

Potassium Iodide (KI):

It is a special chemical, which reduces only copper ions from Cu^{2+} to Cu^+, in the presence of other metal ions in PCB solution. And liberate equivalent amount of Iodine (I_2)
(Reaction given in previous slide)

Estimation of Copper from PCBs e-waste (Waste PCBs: WPCB)

Std. $Na_2S_2O_3$ ('Y'N)



Procedure : Iodometeric method.

The end point of the titration is BLUE to COLORLESS

25ml of PCB solution+ One spatula Urea+ Ammonium hydroxide d/d + 1/2 test tube of Acetic acid + 1 test tube of KI + Starch indicator.

Step (1): Reacting [Cu2+] with KI and liberating I_2

$2Cu + 4KI + H_2SO_4 \longrightarrow I_2 + K_2SO_4 + Cu_2I_2 + 2H^+$

The amount of I_2 liberated is equivalent to [Cu].

Step (2): Reacting I_2 with Std $Na_2S_2O_3$

$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$

Starch (colorless) + I_3^- (Brown) $\longrightarrow$ [Starch- I_3^-]

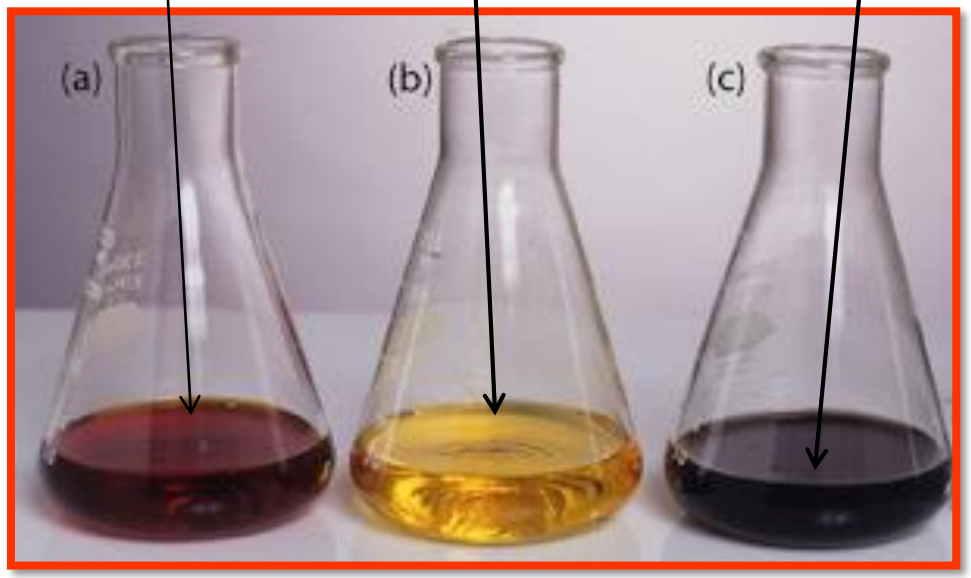
Let the end point of the titration is = 'V' ml. volume of the

Estimation of Copper from PCBs e-waste (Waste PCBs: WPCB)

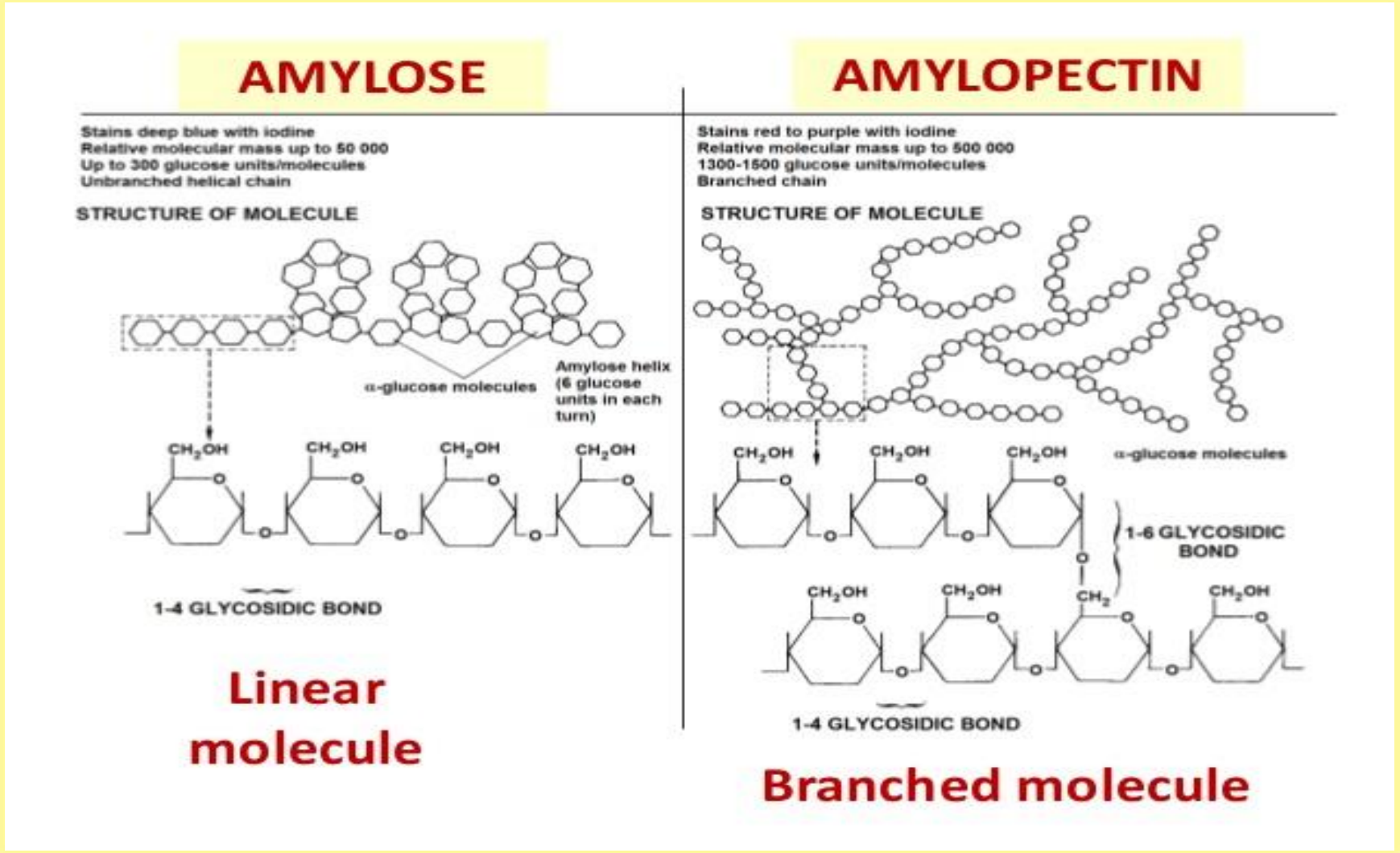
When Iodine (DARK Brown) is liberated, which is equivalent to Cu

When it is titrated with $Na_2S_2O_3$, Iodine reacts and its concentration decreases (Brown color decreases)

When starch indicator is added, Iodine reacts with starch, forms dark blue (violet) solution.



Estimation of Copper from PCBs e-waste (Waste PCBs: WPCB)



Estimation of Copper from PCBs e-waste (Waste PCBs: WPCB)

How it works – Mechanism of Reaction

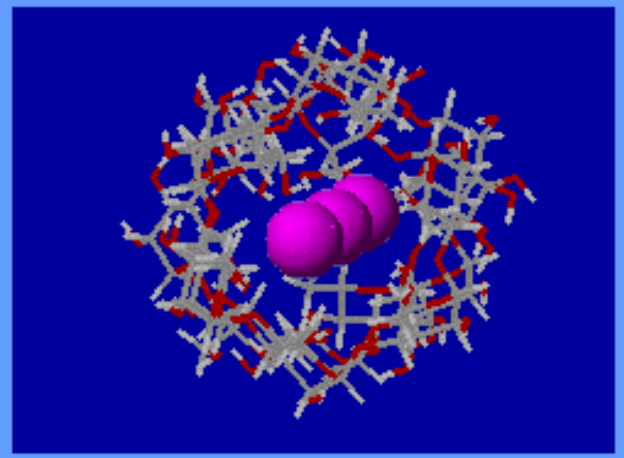
3. The free iodine combines with iodide very rapidly to form the negative ion I_3^-, which reacts with starch to form a dark blue complex:

$$I_2 + I^- \xrightarrow{\text{fast}} I_3^- + \text{Starch} \xrightarrow{\text{fast}} \text{Dark Blue Complex}$$

Amber

Starch - Iodine Complex

$$I_2 + I^- \longrightarrow I_3^-$$



Iodine slides into starch coil
to give a blue-black color

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Observations and calculations:

Note: The equivalent wt of Cu is 63.54 g (The change in oxidation number is 1)

One gram equivalent wt of $Na_2S_2O_3$ = one gram equivalent wt of Copper

i.e, 1000 ml of 1N $Na_2S_2O_3$ = 63.54 g (Eq. Wt.) of Copper

Therefore, 'V' ml of 'Y' N $Na_2S_2O_3$ = **?????**

= (V x Y x 63.54) /1000 **in grams**

i.e, 25 ml of PCB solution titrated contains = (V x Y x 63.54) /1000 **in grams**

Therefore, 1000 ml of PCB solution contains= **????**

= {Vx Y x 63.54} / 25

=……..g/L

The amount of Cu the given 1000 ml of PCB solution is =……g