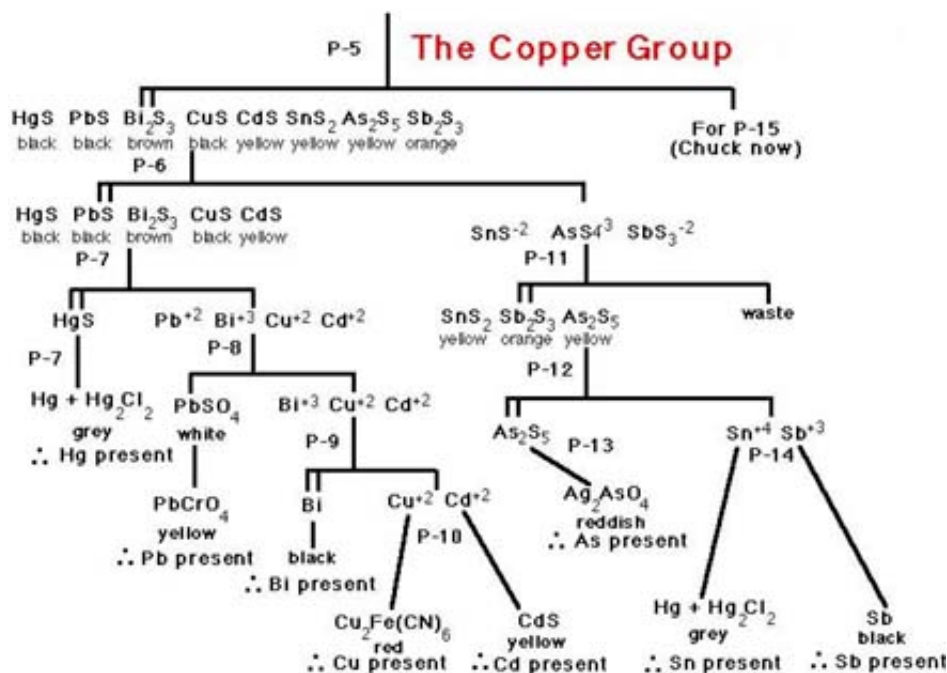


The Copper Group



The Separation of the Copper Group:

Facts: The SULFIDES of Lead, Mercury (II), Bismuth, Copper, Cadmium, Arsenic, Antimony, and Tin are insoluble in dilute HCl. The sulfides of all metals of the following groups are soluble in HCl. Upon this fact is based the separation of the cations of the Copper-Arsenic group from the cations of the following groups.



This is a crucible...

We use it for evaporating solutions.

Procedure 5: Precipitation of the Copper-Arsenic group. Place 4 drops of the **known** [E-9] **OR** the **unknown** [from instructor], (or the decantate from Procedure 1 if you are doing a salt), into a crucible. **[WARNING:** Never mix the **known** with the **unknown** !]. Add 2 drops of 3% H₂O₂ [C-6] and 2 drops of 2 M HCl [A-3]. Carefully evaporate down to a volume of 1 or 2 drops. Allow to cool (**NEVER place hot glassware or crucibles into cold water!**). Then add 6 drops of 6 M HCl [A-2]. Carefully evaporate the contents of the crucible down to a pasty mass, being **VERY CAREFUL NOT TO BAKE** the residue-- **No Brownouts! It's tickle, tickle, git otta there!** Allow to cool.

To the residue in the cool crucible add exactly 4 drops of 2 M HCl [A-3]. Swish the acid around until all of the residue is dissolved; if necessary, stir the mixture and warm slightly. Then transfer the solution to a 10 X 75 mm test tube, add 4 drops of 1 M Thioacetamide solution [in the hood], mix thoroughly, and heat in the boiling water bath for 5 minutes.

Add 8 drops of hot water, 8 drops of 1 M Thioacetamide [in the hood] and 1 drop of 1 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ [B-5], mix well, and heat in the boiling water bath for 5 minutes.

Add 4 more drops of hot water and 8 more drops of 1 M Thioacetamide, mix well and heat in the boiling water bath for 5 minutes. Centrifuge and decant into a test tube.

[If this is a salt analysis, transfer the decantate to a crucible, simmer this decantate, which contains the cations of the groups that follow, for 1 minute and save it for Procedure 15]. (**Chuck it for now**).

Wash the precipitate three times with mixtures of 10 drops of hot water plus 10 drops of 1 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ [B-5] and analyze according to Procedure 6. [The Ammonium Acetate is a strong electrolyte which will coagulate peptized precipitates. Coagulate = glump together (like cottage cheese), Peptized = finely divided so it's hard to settle)].

In this and all future washing operations be sure that the precipitate and washing liquid are well mixed by vigorous agitation with a stirring rod (**don't punch out the bottom of your tube**).

Separation of the Copper Subgroup from the Arsenic Subgroup:

Facts: The sulfides of Arsenic, Antimony, and Tin(IV) are soluble in a solution of Ammonium Sulfide. The sulfides of Copper, Lead, Mercury, Bismuth, and Cadmium are insoluble. This fact is the basis for the separation of the Copper subgroup from the Arsenic subgroup.

Procedure 6: Separation of the Copper subgroup from the Arsenic subgroup:

To the test tube containing the precipitate from Procedure 5, add 10 drops of $(\text{NH}_4)_2\text{S}$ solution [in da hood]. Stir the contents of the tube well; then heat for 4 minutes in the boiling water bath, stirring the contents meanwhile. Avoid heating the tube to the point where excessive frothing of the contents occurs.

Centrifuge, decant into a test tube, and save the decantate, which may contain SnS_3^{2-} , SbS_3^{3-} , and AsS_4^{3-} , for Procedure 11. (**Warning, label this and don't lose it!**).

Repeat the treatment of the precipitate with a second 10-drop portion of $(\text{NH}_4)_2\text{S}$ solution, heating the tube in the boiling water bath and stirring for 2 minutes. Centrifuge and decant, combining the second decantate with the first; save it in a stoppered and **LABELED** test tube for Procedure 11.

Wash the precipitate twice with a mixture of 10 drops of hot water with 10 drops of 1 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ [B-5]; analyze this precipitate, which may consist of the sulfides of Mercury (II), Lead, Bismuth, Copper, and Cadmium, according to Procedure 7.

Separation of Mercury from Lead, Bismuth, Copper, and Cadmium

Facts: The sulfides of Copper, Bismuth, Cadmium, and Lead are soluble in warm dilute HNO_3 . HgS is insoluble. The separation of Mercury from Lead, Bismuth, Copper, and Cadmium is based on this fact.

Procedure 7: Separation and detection of Mercury(II):

Add 15 drops of 3 M HNO_3 [A-6] to the test tube containing the precipitate from Procedure 6, mix thoroughly, transfer to a crucible and simmer gently for 2 minutes. Replenish the HNO_3 when necessary.

Transfer to a test tube, centrifuge, and decant into a test tube, saving this decantate for Procedure 8.

Wash the precipitate twice with 15-drop portions of water made acidic with a drop of 3 M HNO_3 [A-6]. Add the first washing to the decantate in the test tube; discard the second washing.

Treat the precipitate with 6 drops of 12 M HCl [hood] and 2 drops of 16 M HNO_3 [zee hood], mix thoroughly and heat for 1 minute in the boiling water bath. Add 10 drops of hot water, transfer to a crucible, simmer gently for about 30 seconds, and then transfer back to a test tube.

Cool by holding the test tube under the water tap, then centrifuge. To the cool supernatant solution (the liquid above the ppt) in the test tube add 25 drops of 0.2 M SnCl_2 (Stannous Chloride) [E-2] solution. A black (Hg) or gray ($\text{Hg}_2\text{Cl}_2 + \text{Hg}$) precipitate proves the presence of Mercury(II). Note for re-filling: SnCl_2 is called Stannous Chloride.

Separation of Lead from Bismuth, Copper, and Cadmium

Facts: Lead sulfate is insoluble in water. The sulfates of bismuth, copper, and cadmium are soluble, This fact is the basis for the separation of lead ions from bismuth, copper, and cadmium ions.

Procedure 8: Separation and detection of Lead

Add 4 drops of 18 M H_2SO_4 [hood] to a crucible containing the decantate from Procedure 7 and evaporate carefully down to a volume of about 1 drop. At this point dense white fumes of $\text{SO}_3(\text{solid})$ (Sulfur Trioxide) should form. If not add more 18 M H_2SO_4 . **(WARNING: The dense white fumes are solid particles. They should rise up two meters high. Do NOT confuse "steam" which is liquid droplets of water with fumes. Steam will evaporate, solid fumes do not evaporate).** [Have Boom approve your *Dense White Fumes*].

Allow to cool to room temperature, add 15 drops of cold water, swish, and stir the contents until all material in the crucible is dissolved or suspended; then transfer it quickly to a test tube before the suspended material has a chance to settle; swish the crucible with 4 drops of cold water and transfer this washing to the same test tube. Cool under the water tap. A white precipitate, PbSO_4 , should form. This may take a while.

Centrifuge until the supernatant liquid is clear and decant into a test tube, saving this decantate for Procedure 9.

Wash the precipitate twice with 10-drop portions of cold water. To the washed precipitate in the test tube add 4 drops of 1 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ [B-5], and stir for 20 seconds; then add 2 drops of 0.2M K_2CrO_4 [D-1], The yellow precipitate, Lead Chromate, PbCrO_4 , proves the presence of lead.

Separation of Bismuth from Copper and Cadmium

Facts: Addition of NH_4OH to a solution containing Bismuth, Copper, and Cadmium ions first precipitates the hydroxides of all three metals. The hydroxides of Copper and Cadmium, however, dissolve in an excess of NH_4OH , whereas the hydroxide of Bismuth does not.

Procedure 9: Separation and detection of Bismuth

To the decantate from Procedure 8 add 15 M NH_4OH [A-8], dropwise, with constant mixing, until it becomes distinctly alkaline (litmus test). Stir for two minutes. Centrifuge and decant, saving the decantate for Procedure 10.

Wash the precipitate twice with 18 drop portions of hot water. To the washed precipitate add 3 drops of 8 M NaOH [hood] and 2 drops of 0.2 M SnCl_2 [E-2] and stir. A jet-black precipitate (Bi) proves the presence of Bismuth.

Detection of Copper and Cadmium

Procedure 10: Separation and detection of Copper and Cadmium

(A) Detection of Copper.

If the decantate from Procedure 9 is colorless, Copper may be absent. If the decantate is deep blue, because of the $\text{Cu}(\text{NH}_3)_4^{+2}$ ion, Copper is definitely present.

Place 5 drops of the decantate into a test tube. [If it is blue, add 5 M $\text{HC}_2\text{H}_3\text{O}_2$ [A-7] until the deep blue color just disappears]. Add 2 drops of 0.2 M $\text{K}_4\text{Fe}(\text{CN})_6$ [D-3]. A red precipitate ($\text{Cu}_2\text{Fe}(\text{CN})_6$) confirms the presence of copper.

(B) Detection of Cadmium.

Treat the decantate from Procedure 9 with 3 drops of $(\text{NH}_4)_2\text{S}$ solution [hood], mix thoroughly, and allow to stand for one minute. The formation of a yellow precipitate (CdS) proves the presence of Cadmium.

Procedure 11: Reprecipitation of the sulfides of Arsenic, Antimony, and Tin

To the test tube which contains the decantate from Procedure 6 (sure hope you can find it), which contains AsS_4^{-3} , SbS_3^{-3} , and SnS_3^{-3} , add 6 M HCl [A-2], with constant stirring, until the solution shows an acidic reaction with litmus. (As long as each drop of 6 M HCl keeps on bringing down more precipitate, the solution is still alkaline; when no more precipitate forms, the solution is probably acidic). A large excess of HCl must be avoided.

Centrifuge and decant, discarding the decantate. Wash the precipitate three times with a mixture of 5 drops of 1 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ [B-5] (to coagulate peptized ppts) and 5 drops of hot water and analyze according to Procedure 12.

Separation of Arsenic from Antimony and Tin

Facts: Arsenic sulfide is insoluble in concentrated HCl, the sulfides of Tin and Antimony dissolve in HCl.

Procedure 12: Separation of Arsenic from Antimony and Tin

To the precipitate from Procedure 11 add 15 drops of 12 M HCl [hood], mix thoroughly, and heat the test tube in the boiling water bath for 4 minutes, stirring frequently.

Add 7 drops of hot water, mix well and continue heating in the boiling water bath, for another 30 seconds.

Centrifuge, and decant into a crucible. Save this decantate for Procedure 14.

Wash the precipitate once with 10 drops of 6 M HCl [A-2], then three times with a mixture of 5 drops of hot water plus 5 drops of 1 M $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ [B-5].

Analyze the precipitate according to Procedure 13.

Procedure 13: Detection of Arsenic

Add 10 drops of 16 M HNO_3 [in dee hood] to the test tube containing the precipitate from Procedure 12 and heat in the boiling water bath for about one minute or until the original precipitate is disintegrated and a deposit of Sulfur is formed (yellow glob).

Add 5 drops of water, centrifuge, and decant into a crucible, discarding any precipitate that remains in the test tube.

Evaporate the solution in the crucible **very carefully**, to complete dryness. Allow it to cool.

Add 4 drops of 0.2 M AgNO_3 [D-7] and swish around in the crucible for about 10 seconds.

Then add 0.2 M $\text{NaC}_2\text{H}_3\text{O}_2$ [D-8], a drop at a time, with thorough mixing, until a maximum of 30 drops has been added.

A reddish-brown or chocolate-brown precipitate (Ag_3AsO_4) proves the presence of Arsenic.

Procedure 14: Detection of Antimony and Tin

(A) Detection of Antimony. (Redox on a coin). Transfer the decantate from Procedure 12 into a crucible, simmer for one minute to remove all H_2S , then add 5 drops of cold water and mix thoroughly. Place TWO drops of this solution on a clean coin (any coin except a penny). Place TWO grains of **TIN** [E-3] (for re-fill, see the instructor) into this solution. Rapid formation of a black stain (Sb) on the coin proves the presence of **Antimony**.

(B) Detection of Tin. To the remainder of the solution in the crucible add ONE 5 mm piece of aluminum wire [B-4]. Warm gently until the wire has dissolved; then simmer gently for about two minutes or until the black precipitate either has all dissolved or appears not to be dissolving any more, replenishing the solution with 6 M HCl [A-2] if necessary.

Transfer the contents of the crucible immediately to a test tube, cool, centrifuge, and decant. Immediately add 3 drops of 0.2 M HgCl_2 [C-11] solution to the decantate, mix thoroughly, and allow to stand one minute; a white (Hg_2Cl_2) or gray ($\text{Hg}_2\text{Cl}_2 + \text{Hg}$) precipitate proves the presence of **TIN**.

Here Endeth the Copper-Arsenic Group