PROCEDURE FOR ANALYSIS OF GROUP II CATIONS

WEAR YOUR SAFETY GLASSES WHILE PERFORMING THIS EXPERIMENT.

Unless directed otherwise, you may assume that a 10-mL sample contains the equivalent of about 1 mL of 0.1 M solutions of the nitrate or chloride salts of one or more of the Group II cations. If you are working with a general unknown, your sample is the HCl solution decanted from the Group I precipitate and may contain ions from Groups II, III, and IV.

~~**Step 1.** Pour 5 mL of your Group II sample or your general unknown into a 50-mL beaker. Add 0.5 mL 3% H_2O_2, and carefully boil the solution down to a volume of about 2 mL.~~

Start with the HCl solution you saved from Group I

Step 2. ~~Swirl the liquid around in the beaker to dissolve any salts that may have crystallized, and then pour the mixture into a test tube~~. Add 6 M NaOH a little at a time, until the pH becomes 0.5. (The way to accomplish this is discussed in the comments on procedure following this section.) When the pH has been properly established, add 1 mL 1 M thioacetamide and stir.

Heat the test tube in the boiling-water bath for at least five minutes. *CAUTION:* Small amounts of H_2S will be liberated. This gas is toxic, so avoid inhaling it unnecessarily. If any Group II ions are present, a precipitate will form; typically, its color will be initially light, gradually darkening, and finally becoming black. Continue to heat the test tube for at least two minutes after the color has stopped changing. Cool the test tube under the water tap and let it stand for a minute or so. Centrifuge out the precipitate and decant the solution into a test tube. Add 1 mL 1 M NH_4Cl and 1 mL water to the precipitate and put it aside.

Depending on what your unknown is (a I/II or a II/III), choose one of these methods for checking to make sure all the right sulfides precipitated.

Under the conditions described here, cadmium ion will not precipitate if the concentration of Cl^- ion is too high. If CdS does not come down, cadmium will carry over into Group III. *If* your unknown contains only Group II cations, you should force the precipitation of CdS, and any other sulfides that were reluctant to precipitate, by adding 6 M NH_3, drop by drop, to the decanted solution until the solution is basic to litmus. Then add 1 mL 1 M thioacetamide and heat the test tube in the water bath, stirring occasionally, for three minutes. Centrifuge out any precipitate, and decant the liquid, which should be saved only if it contains ions from groups to be studied later. Add 1 mL 1 M NH_4Cl and 1 mL water to the precipitate, stir, and pour the slurry into the test tube containing the first portion of Group II precipitate. Stir well, centrifuge, and decant the liquid, which may be discarded. Wash the precipitate once again with 3 mL water. Centrifuge and discard the wash liquid.

If you are working with a general unknown, containing ions from Groups

III and IV, you cannot make the solution you decanted from the initial sulfide precipitate basic, since that would bring down those groups. Rather, check the pH of the decanted solution. If it is too low (too acidic), add 0.5 M $NaC_2H_3O_2$, sodium acetate, drop by drop with stirring, until the pH is again 0.5. A precipitate may form during this adjustment; usually it is brown or yellow. Add 1 mL 1 M thioacetamide to the mixture, and proceed as in the preceding paragraph, starting with the fourth sentence, the one that reads "Heat the test tube. . . . "

Step 3. To the precipitate from Step 2 add 2 mL 1 M NaOH, *not* 6 M. Heat in the water bath, with stirring, for two minutes. Any SnS_2 or Sb_2S_3 should dissolve. The residue will typically be dark and may contain CuS, Bi_2S_3, PbS, CdS, and HgS. Centrifuge and decant the yellow liquid into a test tube (Label 3). Wash the precipitate twice with 2 mL water and 1 mL 1 M NaOH. Stir, centrifuge, and decant, discarding the wash each time.

Skip to step 13, 14, and 15 in the lab manual to finish your work in the hood.

Step 4. To the precipitate from Step 3, add 2 mL 6 M HNO_3. Heat in the boiling-water bath. Most of the reaction will occur within about a minute, as some of the sulfides dissolve and sulfur is formed. There may be a substantial amount of residue, which is mainly HgS and free sulfur. Continue heating until no further reaction appears to occur, at least two minutes after the initial changes. Centrifuge and decant the solution, which may contain Cu^{2+}, Bi^{3+}, Cd^{2+}, and Pb^{2+}, into a test tube. ~~Wash the residue with 2 mL water, centrifuge, and discard the wash. Then add 1 mL water to the residue and put it aside (Label 4).~~

Step 4 can be done outside the hood.

(there is no Hg)

Step 5. To the solution from Step 4, add 6 M NH_3 until the solution is basic to litmus. Then add 0.5 mL more and stir. If copper is present, the solution will turn blue. A white precipitate in the solution is indicative of bismuth (or, possibly, lead). Centrifuge and decant the solution, which may contain $Cu(NH_3)_4^{2+}$ and $Cd(NH_3)_4^{2+}$, into a test tube. Wash the precipitate with 1 mL water and 0.5 mL 6 M NH_3. Stir, centrifuge, and discard the wash.

Step 6. To the precipitate from Step 5, add 0.5 mL 6 M HCl and 0.5 mL water. Stir to dissolve any $Bi(OH)_3$ that is present. A white insoluble residue may contain lead. Centrifuge and decant the solution into a test tube. Wash the residue with 1 mL water and 0.5 mL 6 M HCl. Centrifuge and discard the wash.

Step 7. *Confirmation of the presence of bismuth* Add 2 or 3 drops of the decantate from Step 6 to 300 mL water in a beaker. A white cloudiness caused by precipitation of BiOCl appears if the sample contains bismuth. To the rest of the decantate, add 6 M NaOH until it is definitely basic; a white precipitate is $Bi(OH)_3$. To the mixture add 2 drops 0.1 M $SnCl_2$ and stir; if bismuth is present, it will be reduced to black metallic bismuth.

This solution must be VERY basic

Step 8. *Confirmation of the presence of lead* To the white precipitate from Step 6, add 1 mL 0.5 M $NaC_2H_3O_2$, sodium acetate. Heat gently if necessary to dissolve any lead-containing salts. Add 1 mL water and 1 mL 3 M H_2SO_4. A white precipitate of $PbSO_4$ establishes the presence of lead.

Step 9. *Confirmation of the presence of copper.* If the solution from Step 5 is blue, copper must be present, since the color is characteristic of the $Cu(NH_3)_4^{2+}$ ion. To further confirm copper(II), add about 0.3 g of solid $Na_2S_2O_4$, sodium hydrosulfite, to the blue solution. It should quickly decolorize as copper(II) is reduced to copper(I). Put the test tube in the boiling-water bath, where further reduction to reddish or black copper metal will occur. After about a minute, centrifuge out the solid and decant the liquid into a test tube. Discard the solid.

Stop here (there is no Cd, Hg, or Sn)

Step 10. *Confirmation of the presence of cadmium.* To the decantate from Step 9 add 1 mL 1 M thioacetamide and heat in the water bath. Precipitation of yellow CdS will occur within a few minutes if cadmium is present.

Step 11. Pour off the water from the precipitate from Step 4 and add 1 mL 6 M HCl and 1 mL 6 M HNO_3. Put the test tube in the water bath. The dark precipitate, which is mainly HgS, should dissolve in a minute or two, leaving some insoluble sulfur residue. Pour the contents of the tube into a 50 mL beaker and boil gently for about a minute. Add 3 mL water to the solution, stir, and pour the liquid into a test tube. Centrifuge out any solid.

Step 12. *Confirmation of the presence of mercury.* Pour half of the liquid from Step 11 into a test tube. Immerse an 8 cm length of copper wire in the liquid for a minute; a shiny deposit of liquid mercury on the wire confirms the presence of mercury. To the other half of the liquid from Step 11, in a test tube, add 3 mL water and stir. Then add 0.1 M KI, potassium iodide, drop by drop, without stirring. If mercury is present, you will get a red-orange precipitate of HgI_2 at the interface between the upper (yellow) KI layer and the lower colorless solution.

Step 13. To the decantate from Step 3 add 6 M HCl drop by drop until the mixture becomes acidic (pH ~ 0.5, green color on methyl violet). The precipitate that forms may contain the sulfides of Sb(III) and Sn(IV). Stir well for half a minute, centrifuge, and discard the liquid.

Step 14. To the precipitate from Step 13, add 2 mL 6 M HCl. Stir and transfer the mixture to a 50-mL beaker. Boil the liquid gently for one minute to drive out H_2S and to dissolve the sulfides. A black residue is mainly HgS. Add 1 mL 6 M HCl and then pour the solution into a test tube. Centrifuge out any solid residue and transfer the liquid to a test tube. Discard the solid.

Step 15. *Confirmation of the presence of tin.* Pour half of the solution from Step 14 in a test tube and add a 1-cm length of 24-gauge aluminum wire. Heat the test tube in the water bath to promote reaction of the Al and production of H_2. In this reducing medium, any tin present will be converted to