

HELPFUL HINTS

PRUDENT PRACTICES

- ❖ Work individually and proceed at your own rate.
- ❖ You are strongly encouraged to set up **collaborative groups** of 3-4 to compare and consult as you go.
 - Think together about reactions and results.
 - Rely on each other to help interpret results. Your group will provide a sounding board for questions like: Is there a precipitate here or not? What color is this? Is this the right color for a positive test? Ooh, that's a weird test result, what does it mean? Does this unknown conclusion make sense? What kind of alternate or blanket test could I run to verify a conclusion?
 - Provides more opportunity to experience the chemistry, more experience in how chemistry (science) is done, and a way to build your confidence in your lab skills and your understanding.
- ❖ Review the "Helpful Hints" and "Safety and Locations" handouts each day to ensure you don't miss essential details.

LAB PROCEDURES SUMMARY

- ❖ Measuring liquid: don't use a graduated cylinder, count drops.
 - When held near vertically, the dropping bottles give about 10-40 drops/mL depending on the bottle top.
 - The more horizontally the bottle is held, the larger the drops produced.
- ❖ Measuring solids: don't weigh it out, use a small amount on the end of a spatula.
- ❖ Adjusting pH - use litmus paper to test.
 - If it is the wrong color before testing, hold it over con HCl (turns red) or con NH₃ (turns blue).
- ❖ Testing for complete precipitation - add reagent, stir, heat and wait, centrifuge, add a bit more reagent.
- ❖ Washing solids - add solution, stir, centrifuge, decant.
- ❖ Separate solid from liquid - decant (pour off) the liquid and leave solid behind, touch off the last drop - alternately, use a dropper to remove the liquid.
 - "Floaters" that typically stay with the decantate are not a problem.
 - Likewise, leaving a drop of solution behind with the precipitate is not a problem if you have washed the precipitate thoroughly.
- ❖ Transfer a solid as a slurry - that's not quantitative, but good enough.
- ❖ Storing solutions and precipitates.
 - Stopper test tubes.
 - Label test tubes clearly.
 - Document everything in your notebook.
- ❖ Evaporation - use the casserole, under the hood if noxious fumes are produced.

FOR ALL QUAL GROUPS

- ❖ Make sure you completely precipitate each group. Any carryover to the next group will cause problems!!!! This is especially important for the alloys and solid salts because it is easy to get high concentrations when you are making your own solutions.
- ❖ **Keep test tubes, droppers, casserole, stirring rods, beakers clean. Contamination will kill you.**
- ❖ The qual scheme is a systematic approach that is a good start for identifying the composition of an unknown. But don't feel tied to the qual scheme. After you know something about what's present and what's absent, use your knowledge of the chemistry to devise "short cuts" and spot tests to double check results or clarify tests you are not sure about. For cations, NH₃ and OH⁻¹ complex formation can be very helpful. Adding (NH₄)₂S dropwise to decantates and observing precipitate colors can provide even more information.
- ❖ **DISPOSAL OF SPENT REAGENTS:**
 - Collect all known and unknown residues in appropriate receptacle under the hood. **DO NOT DUMP** these down the drain.
 - **USE AND DISPOSE OF KCN SOLUTIONS ONLY IN THE HOOD. DO NOT ACIDIFY KCN SOLUTIONS!!!**

Cu-As GROUP

- ❖ ID of Sb with S₂O₃⁻² is sometimes tough to see (small amount of ppt). When reacting with Al wire in the previous step, look for a black ppt that does not redissolve in the acid. This ppt is an indication of Sb (assuming you don't have contamination from cations that were supposed to be removed at this point). If thiosulfate does not confirm presence of Sb, double check.

- ❖ $K_4Fe(CN)_6$ is slowly oxidized in air. Potassium ferricyanide [$K_4Fe(CN)_6$] is a very pale yellow; potassium ferri-cyanide [$K_3Fe(CN)_6$] (oxidation product) is a more intense yellow. If the reagent gets too yellow, notify the instructor to replace it.
- ❖ Sulfur is typically a curdy precipitate that comes in a range of colors from off-white to yellow to darker shades and is formed in a variety of reactions in the qual scheme - sulfides reacting with HNO_3 , acidification of the polysulfides in $(NH_4)_2S$, etc. - and may appear even when no cations are present. This sulfur has a distinct texture and behavior that are different from other precipitates encountered in the cation scheme. Learn to recognize it so you don't confuse it with evidence for presence of cations.
- ❖ **WORK WITH KCN ONLY IN THE DESIGNATED HOOD.**
- ❖ **DO NOT ACIDIFY SOLUTIONS CONTAINING KCN.**
- ❖ **PUT ALL CYANIDE CONTAINING SOLUTIONS INTO THE COLLECTION BEAKER PROVIDED IN THE DESIGNATED HOOD.** Periodically, the instructor will destroy the cyanide with bleach and dispose of it.
- ❖ **KEEP ACIDS OUT OF THE HOOD DESIGNATED FOR KCN USE - DO NOT ACIDIFY SOLUTIONS IN THIS HOOD.**
- ❖ Presence of Cu^{+2} readily masks the confirmation test for Cd^{+2} . Make sure you add an excess of KCN in the detection of Cd. If a black ppt forms (CuS), you can easily recover without starting completely over. Completely precipitate the CuS and any CdS with $(NH_4)_2S$. Centrifuge and decant from the KCN. Redissolve the ppt in hot HNO_3 , remove the sulfur ppt, add NH_3 to neutralize the acid and form the ammonia complexes again. This brings you back to the beginning of the Cd test step.
- ❖ Be alert for a possible problem with the KCN solution: Stoichiometrically, the amount of KCN required should be in the ratio 5 CN:2 Cu, plus a bit extra to drive the equilibrium for complex formation. When the $[Cu^{+2}]$ in the original known or unknown is ~ 0.2 M (cation solutions), then it should take roughly 10-15 drops of KCN. If significantly more KCN is required to mask the Cu for a Cd test, notify the instructor. (Remember that $[Cu^{+2}]$ in the alloy and single salt solutions depends on how you make the solution, so the guideline set here may not apply in those cases.)

Al-Ni GROUP

- ❖ The confirmation test for Al forms a "red lake." A "lake" is formed when a dye adsorbs to a precipitate. The compound color is **not** changed, it is covered by the color of the dye. Other precipitates that adsorb the dye will form a similarly colored lake and can thus interfere.
- ❖ So, make sure Cr^{+3} (green or violet) is **COMPLETELY** converted to CrO_4^{-2} (yellow) before testing for Al. Cr^{+3} gives a positive Al test (same colored lake).
- ❖ Zinc tests given in the text do not work all that well. Use the following Zn test instead.

Alternate test for Zinc: Substitute this test for Procedure 22 A or C (as appropriate).

Add con H_2SO_4 to the decantate until it's barely acidic and then add 1 more drop. To the mixture add 1-2 drops of 0.025 M $CuSO_4$ and mix well. If a white precipitate forms ($BaSO_4$), add $(NH_4)_2SO_4$ until precipitation is complete; centrifuge and decant. To the decantate add 5-6 drops of 0.18 M $(NH_4)_2[Hg(SCN)_4]$ (ammonium mercuri-thiocyanate or more formally ammonium tetrathiocyanatohydrargyrate (II) - mercurate is also acceptable terminology here). Presence of a blackish-purple precipitate confirms the presence of Zn^{+2} . If the solution is not distinctly acidic, a green precipitate ($Cu[Hg(SCN)_4]$) will form when Zn is absent.

The underlying chemistry:

Excess Ba(II), added to precipitate chromate in the previous step, will precipitate with the sulfate added in this step. Make sure all the Ba(II) is precipitated, and then remove the white precipitate so it won't be confused with any precipitate from the mercuri-thiocyanate.

$Hg(SCN)_4^{-2}$ is a stable complex ion that will precipitate with most other cations. $Zn[Hg(SCN)_4]$ is white and is *insoluble* in acid while $Cu[Hg(SCN)_4]$ is green and is *soluble* in acid. However, when both cations are present together, they co-precipitate to form a violet or blackish-purple precipitate that is not soluble in acid.



This test can be inserted directly into the qual scheme from our text for the confirmation of zinc since all other cations (possible interferences) have been removed at that point.

- ❖ Sulfides of this group are notorious for forming colloidal suspensions that are hard to make settle out. Usually you can get enough to centrifuge out to do the testing for this group, unsettled precipitate will be removed in the first step of the Ba-Mg group.
- ❖ If you encounter an unknown that will not centrifuge down enough to do the Al-Ni group testing, do the first step of the Ba-Mg group (bake down) and work with the **precipitate** recovered from that step.

Ba-Mg GROUP

- ❖ The confirmation test for Mg forms a “blue lake.” A “lake” is formed when a dye adsorbs to a precipitate. The compound color is **not** changed, it is covered by the color of the dye. Other precipitates that adsorb the dye will form a similarly colored lake and can thus interfere.
- ❖ The confirmation test for Mg^{+2} with phosphate is tricky; i.e. very pH dependent. Follow the directions for amounts **carefully**.
- ❖ Several ions, including some not in the Ba-Mg group, produce a colored flame:
 - Ba - green
 - Ca - red-orange, sometimes similar to Na but less persistent (fades sooner).
 - Na - fluffy yellow, intense enough to cover any other colors.
 - K - violet, not very intense.
 - Cu - blue green flame similar to, but distinct from Ba.
 - Sn - light blue - similar to, but distinct from K.
 - B - green, similar to Ba. B may be present as borate.
 - Li - red (intense), distinctly different from Ca.
 - Sr - red, similar to Li and intense.
- ❖ Na^+ is everywhere. Test for Na on the original sample. Look for a persistent flame test, not a spotty or fading color. Note that sodium is a common impurity in most chemicals and that glassware has a sodium component that is slowly leached out so you will probably see some sodium in everything you test. Learn to distinguish between an impurity and an actual component.
- ❖ $BaSO_4$ is very insoluble so it is difficult to see the flame test. Make sure you take a little of the solid for the test. In general, the presence of a ppt is sufficient for ID of barium, the flame test just makes sure that it is not a carryover of lead.
- ❖ For the K flame test, use the Cobalt (blue) glass to filter out the Na flame so you can see the violet K flame. Make sure the glass is thick enough to effectively filter out the Na flame. Use two pieces of glass if necessary. Experiment with the known K solution to determine the thickness required. Be alert, flame tests for lower concentrations of K are hard to detect.
- ❖ In a positive test for NH_4^+ , the litmus paper will give a **uniform** change to the blue color. If the color change appears as a polka dot pattern of blue spots on the red paper, it is due to splattering of the boiling NaOH and **not** a positive test for NH_4^+ .

ANIONS

- ❖ Use CH_2Cl_2 (methylene chloride) instead of carbon tetrachloride for the halogen tests. You only need enough to form a distinctly visible layer in the bottom of the test tube.
- ❖ $FeSO_4$ is slowly oxidized by air. This solution should be a greenish-blue color. If it turns yellow (Fe^{+3}) notify the instructor to replace it.
- ❖ KNO_2 and Cl_2 solutions degrade with time and there is no visible indicator. The instructor plans to replace these solutions weekly. However, it would be a good idea to test each reagent with a known to make sure that it is still working correctly.
- ❖ Recognize that Ag_2SO_4 and $AgC_2H_3O_2$ are sparingly soluble salts, so, if the anion concentration is high enough, they may precipitate in the $AgNO_3$ blanket test.
- ❖ When removing I^- , Br^- , S^{2-} , and CrO_4^{2-} with $Pb(OAc)_2$, recognize that a yellow ppt can be $PbCrO_4$ and/or PbI_2 .
- ❖ Sulfite is readily oxidized to sulfate by air, so all sulfite solutions will have some sulfate present. Learn to distinguish between sulfate as an oxidation product and an ion present in the original solution.
- ❖ Sulfide is also oxidized by air to a variety of products including sulfate and disulfide (S_2^{2-}). Learn to distinguish between sulfate as an oxidation product and an ion present in the original solution. In acid disulfide disproportionates into sulfide (S^{2-}) and elemental sulfur (S) which precipitates as a white or off-white solid.
- ❖ The $Ba(OH)_2$ test for carbonates can be a bit tricky, so carefully watch for bubbling when acid is added to the unknown. Only carbonate and sulfite will produce such bubbling, and sulfite will bubble **only** in concentrated acid.
- ❖ The borate flame test disappears quickly and varies in intensity depending on concentration. Observe carefully and quickly.

- ❖ The fruity odor in the acetate test is similar to, but distinct from, the odor of the ethyl alcohol reagent. Be sure not to confuse the two. An alternate test for acetate is to evaporate the solution to dryness and then bake over a Bunsen burner flame (~1" blue cone, heat at least 2-3 min). Acetate will char and produce a corresponding odor of something burning. Chromate will also give the appearance of charring without the odor due to formation of Cr^{+3} . The "char" from Cr should dissolve in dilute HCl, but the acetate char (C) will not.
 - Make sure the casserole is clean - acetate from previous tests or soap residue will char.
- ❖ You do not have to make the lead acetate test paper for the sulfide test; it is available with the solid reagents. Moisten the test paper before use (H_2S dissolves in water and reacts with aqueous Pb^{+2}).

ALLOYS, SINGLE AND MIXED SALTS

- ❖ The procedure in the text says to dissolve the alloy in aqua regia. You can learn a little more about your alloy if you add the acids separately. First try to dissolve the alloy in HCl with heating - metals more active than hydrogen will dissolve, others will not. Then add HNO_3 to form the aqua regia which should dissolve the alloy completely.
- ❖ Some alloys contain non-metal components (C, P, etc.) which will not dissolve in aqua regia. Black specs that will not dissolve are likely to be these components.
- ❖ Strive to keep concentrations in the dissolved alloy similar to the solutions used up to this point - 0.1-0.2 M. Compare colored solutions to the knowns and dilute until colors have about the same intensity. Higher concentrations require extra work to get complete precipitations or complete reactions and can generate unusual colors.
- ❖ Since concentration of components will vary in alloys, observe each test carefully and be alert for positive tests for trace components.
- ❖ Blanket tests with NH_3 and OH^{-1} , looking at precipitates and complex formation can be very helpful. Adding $(\text{NH}_4)_2\text{S}$ dropwise to decantates and observing precipitate colors can provide even more information. In situations when you have added a strong acid to create the solution, you have to add enough reagent to neutralize the acid and then an excess to see complex or precipitate formation. You may have to centrifuge and decant off excess solution or boil off some water before you can get enough reagent to create the complex.
- ❖ Be on the alert for hydroxy complexes not seen previously. In solutions where concentrations may be higher than 0.2 M, Fe^{+3} , Cu^{+2} , and Co^{+2} can also form colored hydroxy complexes.
 - $\text{Fe}(\text{OH})_6^{+3}$ is a light lavender color
 - $\text{Cu}_x(\text{OH})_{2x-2}^{+2}$ is a blue color
 - $\text{Co}(\text{OH})_4^{+2}$ is a deep blue color

MORE ON SINGLE AND MIXED SALTS

- ❖ The mixed salts are heterogeneous in nature, make sure you get a representative sample of all the parts for your tests.
- ❖ As you make solutions of the salts, strive to keep concentrations in the ranges used up to this point - 0.1-0.2 M. Compare colored solutions to the knowns and dilute until colors have about the same intensity. Higher concentrations require extra work to get complete precipitations or complete reactions and can generate unusual colors.
- ❖ Dissolving salts, even soluble salts, can be a slow process. Try gentle heating and have patience before you decided something is not soluble.
- ❖ Since concentration of components may vary somewhat in solid unknowns, observe each test carefully and be alert for positive tests for lower concentration components. Unlike alloys, trace components in the solid salt unknowns encountered in this course are usually from impurities. But the "intensity" of a test depends on the starting concentration and how efficiently it was retained in each separation step. Learn to distinguish between a positive test and a trace test from an impurity.
- ❖ When testing for the anions in a salt or salt mixture, start with the cold, con H_2SO_4 test. Then make a solution and do blanket or specific tests as necessary.
- ❖ If the mixed salt is not completely soluble in water or acid, work with the solution and the precipitate **separately**. Use the Na_2CO_3 procedure for getting everything into solution only as a last resort; it does not work as well as the procedure indicates.
- ❖ Correction note for p 255: In step III A, Mn^{+2} should **not** be in that list. Mn^{+2} solutions are virtually colorless at the concentrations we are using.