The Analysis of Salts

The Analysis a salt consists of two parts, identification of the cation (Procedures 1-27) and the identification of the anion using the tests in Chapter 8.

Keep in mind that there is no perfectly pure salt. There will be impurities. So when you run your tests, expect to fine some weak (wimpy) tests. Make note of them but be on the lookout for the strong tests. For example, if your salt is NaCl, you will find some K and Mg as impurities but the Na test should be much stronger.

There is no flow sheet for anions. You may take this printout into the lab.

There is no *Known* to do. When you are ready, obtain your salt from the Boom.

The Summary of Steps

I. Examine the solid and note its distinctive and significant physical properties. Procedure 29.

II. Put the solid into solution. Procedure 30. See the on line ***Solubility Rules.***

III. Determine what cations are present. (Procedures 1-27). This time we will **not** "Chuck it" when directed to save for the next group. We flow all the way through. *Follow the yellow brick road*.

IV. Determine which anions are present.

..... A. Observe the color of the solution.

..... B. Determine whether or not any anions can be eliminated on the basis of the results of the cation analysis.

..... C. Treat the solid salt with 18 M H_2SO_4.

..... D. Treat a solution of the salt with $AgNO_3$.

..... E. Treat a solution of the salt with $BaCl_2$.

..... F. Perform specific test for the anions that have not been definitely eliminated or verified as present by the above.

Here we go!

I. Examine the solid and note its distinctive and significant physical properties.

Procedure 29.

Examine the unknown carefully , noting the color or colors and whether the material is crystalline or noncrystalline, homogeneous or heterogeneous. Record your observations.

Certain metals form colored salts. Certain anions have characteristic colors.

Chromate yellow, dichromate orange, permanganate violet, nickel ions green, ferrous ions reddish, chromium ions green to blue to black, cuprous ions blue to green to brown, cobalt ions, wine red to blue, manganese ions gray green.

II. Put the solid into solution. See the on line ***Solubility Rules.***

Procedure 30: **Dissolving the solid:**

(A) Test a bit of the solid with 20 drops of water, first cold, then hot, to see if it will dissolve. If it is completely dissolved, prepare a stock solution by dissolving a quantity the volume of two drops of water in 5 ml. of water and use this solution for cation analysis, preliminary tests for anions, and specific tests for anions. Note the color of the solution.

(B) If the solid is not soluble in water, prepare a solution for cation analysis by dissolving in HCl or $HN0_3$, or, if necessary, in aqua regia. First try 6 M HCl [A-2], then 12 M HCl [hood], followed by dilution with an equal volume of hot water; then try 16 M $HN0_3$ [hood], followed by dilution with water. Finally try aqua regia, 3 drops of 12 M HCl (hood) and 3 drops of 16 M HNO_3. Heat cautiously. Careful!

(C) If the solid is not soluble in water, prepare a solution for anion analysis as follows. Place in a crucible a quantity of the solid the volume of two drops of water; then add 5 ml. of a saturated solution of Na_2CO_3[salts rack] and boil gently for two minutes. Transfer to test tubes, centrifuge, and decant, discarding the precipitate (carbonates of metals). A part of this decantate can be saved for making specific tests for all anions except carbonates. Transfer the remainder of the decantate to a crucible, make acidic with 3 M HNO_3 [A-6], and boil gently until all CO_2 (bubbles) has been driven off. This solution can be used for the group tests with $AgNO_3$ and $BaCl_2$ and for the specific tests for all anions except nitrate, sulfide, sulfite, sulfate, and carbonate.

III. Determine what cations are present.

Procedures 1-27:

Take the solution you have prepared above and do **Procedures 1-27**. This time we will **not** "Chuck it" when directed to save for the next group. We flow all the way through. *Follow the yellow brick road.*

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IV. Determine what anions are present.

Procedure 32. **Analysis for anions:**

Using the solution prepared in P-30 and samples of the solid unknown, make a complete anion analysis in the following order:

1. Make a list of the anions that can be eliminated on the basis of the solubility of the solid (See the on line ***Solubility Rules.***) and the color of the solution.

2. Carry out the three preliminary tests described in Procedure 33, Procedure 34, and Procedure 35.

List the anions definitely eliminated by these tests. List also the anions definitely proved present by these tests.

3. Carry out specific tests (Procedures 36-48) for those anions not definitely proved to be either absent or present by Step 1 or Step 2.

Summarize the results of the cation and anion analyses.

Reactions of salts with cold 18 M H_2S0_4:

These have ***No Reaction:*** Acetate , sulfate , phosphate , borate (BO_3^{-3}) , arsenate , nitrate.

These react:

Chloride: Effervescence, The gas evolved is colorless, has sharp odor, fumes in moist air, turns blue litmus red.

Bromide: Effervescence. The gas evolved is brown, has characteristic sharp odor, fumes in moist air, turns blue litmus red.

Iodide: Effervescence. Solid turns dark brown instantly, slight evolution of gas which fumes in moist air, odor of H_2S, violet fumes of iodine.

Sulfide: Effervescence. Odor of H_2S gas (rotten eggs), free sulfur (yellow) deposited.

Carbonate: Effervescence. Colorless, odorless gas.

Sulfite: Effervescence. Colorless gas with a sharp, choking odor.

Chromate: Color changes from yellow to orange red.

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Procedure 33: Treatment of the Solid with H_2SO_4.

Place in a small test tube as much of the solid as can be carried on 5mm of the tip of the spatula. Add one or two drops of 18 M H_2S0_4 [hood]. Notice everything that happens, particularly the color and odor of escaping gases. (Do not place your nose over the mouth of the test tube but fan any gas toward your nose held a few centimeters away.) Then heat, but not so strongly that the H_2S0_4 is boiled, and note what happens. Finally heat the sides of the test tube over its entire length and note whether or not brown fumes (NO_2) are formed. Do not look down into the test tube. Do not point the test tube at yourself or at your neighbor!

List all anions whose presence or absence is indicated by this test: See ***These react*** above.

Treatment of a Solution of the Anions with $AgNO_3$.

The silver salts of all thirteen anions except nitrate, acetate, and sulfate are insoluble in water. $AgN0_3$ is very soluble, Ag_2S0_4 is moderately soluble, and $AgC_2H_30_2$ is sparingly soluble. The insoluble silver salts have the following characteristic colors: AgCl, white; AgBr, cream; AgI, pale yellow; Ag_2S, black; Ag_3As0_4, chocolate brown; Ag_3P0_4, yellow; Ag_2Cr0_4, brownish red; Ag_2C0_3, white; Ag_2S0_3, white; $AgB0_2$, white or light tan.

AgC1, AgBr, AgI, and Ag_2S are insoluble in dilute $HN0_3$. Ag_2CrO_4, Ag_3As0_4, Ag_3P0_4, Ag_2C0_3, Ag_2S0_3, and $AgB0_2$ are soluble in dilute $HN0_3$. Accordingly, if silver ions, in the form of a solution of silver nitrate, are added to water solutions containing the 13 anions, the 10 insoluble silver salts listed above will precipitate. $AgC_2H_30_2$ may precipitate if the concentration of acetate ions is fairly high. If each precipitate is, in turn, treated with dilute $HN0_3$, all but AgCl, AgBr, AgI, and Ag_2S, will dissolve readily. If the solution containing the anions is acidified with dilute $HN0_3$ before addition of $AgN0_3$, only AgCl, AgBr, AgI, and Ag_2S will precipitate.

Procedure 34: Treatment of the solution of the anions with $AgNO_3$.

If the salt is completely soluble in water, follow (A). If the salt is not soluble in water, follow (C).

(A) The salt is soluble in water Place 10 drops of the water solution in a test tube; then add 4 drops of 0.2 M $AgN0_3$. (D-7). If no precipitate forms, $C1^{-1}$, Br^{-1}, I^{-1}, S^{-2}, AsO_4^{-3}, $P0_4^{-3}$, CrO_4^{-2}, CO_3^{-2}, SO_3^{-2}, and BO_2^{-1} are shown to be absent. If a precipitate forms, any or all these anions may be present; if the precipitate is white, Br^{-1}, I^{-1}, S^{-2}, $As0_4^{-3}$, PO_4^{-3}, CrO_4^{-2}, and, possibly, CO_3^{-2}, are absent but the others may be present; if the precipitate is black, all 13 anions may be present, since black will cover up all other colors. Note the color of the precipitate and try, by means of the list given above, to decide what it is.

Centrifuge and decant, discarding the decantate. Wash the precipitate in the test tube once with cold water; then treat it with a few drops of 3 M $HN0_3$ [A-6] and stir. If the precipitate dissolves completely, Cl^{-1}, Br^{-1}, I^{-1}, and S^{-2} are absent. If the precipitate is not completely dissolved, one or more of the four anions just enumerated is present. Note the appearance of the residue and try to decide what it is. Centrifuge and decant into a test tube.

Save the decantate for Part (B).

(B) Make the decantate from Part (A) just alkaline with 15 M NH_40H [A-8], then make it just acid with 5 M $HC_2H_3O_2$ (acetic acid) [A-7], and add a few drops of 0.2 M $AgNO_3$ [salts rack]. The following precipitates will form if the required anions are present: Ag_2CrO_4, brownish red; Ag_2AsO_4 chocolate brown; Ag_3PO_4 yellow; $AgB0_2$, white or light tan; Ag_2SO_3, white.

On the basis of the observations made in (A) and (B), what anions, if any, are definitely shown to be absent? What anions are shown to be present?

(C) The salt is not soluble in water. A solution, for use in this Procedure and also in Procedure 35, must first be prepared as directed in Procedure 30.

Place 10 drops of this solution in a test tube, acidify with 3 M $HN0_3$ [A-6], and then add 4 drops of 0.2 M $AgN0_3$ [D-7]. If no precipitate forms, $C1^{-1}$, Br^{-1}, I^{-1}, and S^{-2} are absent. If a precipitate forms, it may be AgCl, AgBr, AgI, and Ag_2S. Note the color of the precipitate. On the basis of the observations made in (C), what anions, if any, are definitely shown to be absent? What anions are shown to be present?

Treatment of a Solution of the Anions with $BaCl_2$.

$BaCl_2$, $BaBr_2$, BaI_2, BaS, $Ba(C_2H_30_2)_2$, and $Ba(NO_3)_2$ are soluble in water and in alkaline solution. $BaS0_4$, $BaS0_3$, $BaC0_3$, $BaCr0_4$, $Ba_3(As0_4)_2$, $Ba_3(P0_4)_2$ and $Ba(B0_2)_2$ are insoluble. $BaS0_4$ is insoluble in strong acids, such as dilute $HN0_3$ or dilute HCl; the other water-insoluble barium salts are salts of weak acids and are therefore soluble in dilute HNO_3 or dilute HCl. These facts are the basis for the use of barium chloride as a reagent for the elimination of anions. $BaCr0_4$ is yellow; the other barium salts are white.

Procedure 35: Treatment of a solution of the anions with $BaCl_2$.

If the salt is soluble in water, use the water solution, if the salt is not soluble in water, use the solution prepared as directed in Procedure 30.

Place 5 drops of this solution in a test tube, make just alkaline with 5 M NH_4OH [A-9], and mix thoroughly. If any precipitate forms (hydroxides of metals), centrifuge and decant into a clean test tube, discarding the precipitate. Treat the decantate or solution with 3 drops of 0.2 M $BaCl_2$ [salts rack]. Formation of a precipitate shows the presence of one or more of the following anions: SO_3^{-2}, $S0_4^{-2}$, $C0_3^{-2}$, CrO_4^{-2}, BO_2^{-1}, PO_4^{-3}, AsO_4^{-3}. A yellow precipitate proves the presence of chromate; a white precipitate proves the absence of chromate. Make the mixture acid with 2 M HCl [A-3] and stir well. If the precipitate dissolves completely, the absence of sulfate is proved. If the precipitate is not completely dissolved by HCl, the presence of sulfate is proved.

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Specific Tests for Anions

Omit Procedure 36: Test for the arsenate ion (AsO_4^{-3})

Procedure 37: Test for the phosphate ion (PO_4^{-3})

Place 5 drops of the solution in a test tube, acidify with 3 M $HN0_3$ [A-6], add 4 drops of ammonium molybdate solution [$(NH_4)_2Mo0_4$] [salts rack], mix thoroughly, and heat in the boiling water bath for 2 minutes. Formation of a finely divided yellow precipitate [$(NH_4)_2Mo0_4 \bullet 12\ Mo0_3$ confirms the presence of the phosphate ion.

Procedure 38: Test for the borate ion ($B0_3^{-3}$ or BO_2^{-1})

Place a small quantity of the solid material in a crucible, add 4 drops of 18 M H_2S0_4 [hood], and stir thoroughly. Then add 10 drops of methanol (CH_30H) [salts rack] and again mix thoroughly; then set fire to the mixture (neat). Do not stir after the mixture has taken fire. If it burns with a green flame the instant that it takes fire, the borate ion is present. A green flame that does not appear until 20 or 30 seconds after the mixture has taken fire, or unless the mixture is stirred while on fire, is due to copper or barium and should be ignored.

Procedure 39: Test for the chromate ion (CrO_4^{-2})

Place two drops of the solution in a test tube, add 10 drops of water and make just acid with 3 M $HN0_3$ [A-6]. Add 6 drops of ether (ethoxyethane) [salts rack] and 1 drop of 3% H_2O_2 [C-6], stir well, and then allow to settle. A blue coloration of the ether layer confirms the presence of the chromate ion.

Procedure 40: Test for the sulfate ion (SO_4^{-2})

Place a few drops of the solution in a test tube, acidify with 6 M HCl [A-2], and then add a drop of 0.2 M $BaCl_2$ [salts rack]. A white precipitate ($BaSO_4$) proves the presence of sulfate.

Procedure 41: Test for the sulfite ion (SO_3^{-2})

Place 8 drops of the solution in a test tube, acidify (litmus) with 6 M HCl [A-2], add 3 drops of 0.2 M $BaCl_2$ [salts rack], and mix thoroughly. If a precipitate ($BaS0_4$) forms, remove it by centrifuging and decanting. To the clear decantate add a drop of 3% H_2O_2 [C-6]. The formation of a white precipitate ($BaS0_4$) proves the presence of sulfite.

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Procedure 42: Test for the carbonate ion (CO_3^{-2})

Place a small amount of the solid in a test tube. Then add a few drops of 2 M HCl. Test the escaping gas for CO_2 by holding a drop of barium hydroxide solution [A-11], suspended from the tip of a medicine dropper, a short distance down into the mouth of the test tube. The "clouding" of the drop, due to the formation of a white precipitate of barium carbonate ($BaC0_3$), proves the presence of carbonate.

Procedure 43: Test for the sulfide ion (S^{-2})

Place a small quantity of the solid in a test tube and add 10 drops of 6 M HCl. Hold a strip of paper towel moistened with 0.2 M $Pb(C_2H_30_2)_2$ solution [salts rack] over the mouth of the test tube so that any gas that is being evolved will come in contact with the lead acetate. A brownish-black or silvery black stain (PbS) on the paper confirms the presence of sulfides.

If no blackening of the lead acetate occurs after 1 minute heat the tube gently; if still no reaction occurs add a small amount of granulated zinc [salts rack] to the contents of the tube. If the lead acetate is not darkened, the sulfide ion is absent; if it is darkened, sulfide is present.

Procedure 44: Test for the iodide ion (I^{-1})

Place 5 drops of the solution in a test tube and acidify with 5 M $HC_2H_30_2$ [A-7]. Then add 2 drops of 0.2 M $KN0_2$ [salts rack]. A reddish-brown coloration, due to liberation of iodine, proves the presence of iodide. If the brown color is very faint, add a few drops of carbon tetrachloride, (CCl_4) [salts rack], shake, then allow to settle. A violet coloration in the CCl_4 layer shows the presence of iodine. *Ah, polar and non-polar molecules*.

Procedure 45: Test for the bromide ion (Br^{-1})

Place 5 drops of the solution in a test tube; add 5 drops of chlorine water [salts rack]. A brown coloration, due to liberated bromine, shows the presence of bromide. If the solution is shaken with a few drops of CCl_4 [salts rack], the brown color will concentrate in the lower CCl_4 layer. *Ah, polar and non-polar molecules.*

Procedure 46: Test for the chloride ion (Cl^{-1})

Place 6 drops of the solution in a test tube, acidify with 3 M HNO_3 [A-6], and add a drop of 0.2 M $AgN0_3$ [salts rack]. A white, curdy precipitate (AgCl) proves the presence of chlorides.

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Procedure 47: Test for the nitrate ion (NO_3^{-1})

Place 2 drops of the water solution, or the supernatant liquid obtained by treating the solid with hot water in a test tube and carefully add 10 drops of l8 M H_2SO_4 [hood]. Mix well and cool. Carefully add 4 drops of O.2 M $FeSO_4$ solution [salts rack], allowing the latter to float on top of the sulfuric acid solution. Allow to stand for one or two minutes. A brown coloration at the junction of the two layers due to the presence of the complex nitrosyliron(II) ion, $Fe(NO)_2^{+2}$, proves the presence of nitrate.

Procedure 48: Test for the acetate ion ($C_2H_30_2^{-1}$)

Place a small amount of the solid in a test tube, add 3 drops of 18 M H_2SO_4 [hood], and mix thoroughly. Add 4 drops of ethanol (C_2H_5OH) [salts rack], and again mix thoroughly. Heat the tube in the boiling water bath for about 1 minute. Carefully smell the odor of the escaping fumes. A fruity odor, due to ethylethanoate (an ester) ($C_2H_5C_2H_30_2$) (ethyl acetate), proves the presence of acetate. If the test is doubtful, place a pinch of the solid in a test tube, heat strongly, and note whether or not there is any charring of the material. Charring is indicated by the escape of fumes that have the sharp penetrating odor of burned hair or singed feathers; also, the solid darkens in color. Charring shows the presence of acetate.

Here Endeth the Analysis of Anions