Introduction:

Definitions:

Analytical chemistry: Involves separating, identifying, and determining the relative amounts of the components making up a sample of matter.

Qualitative analysis: Identifying the components of a sample.

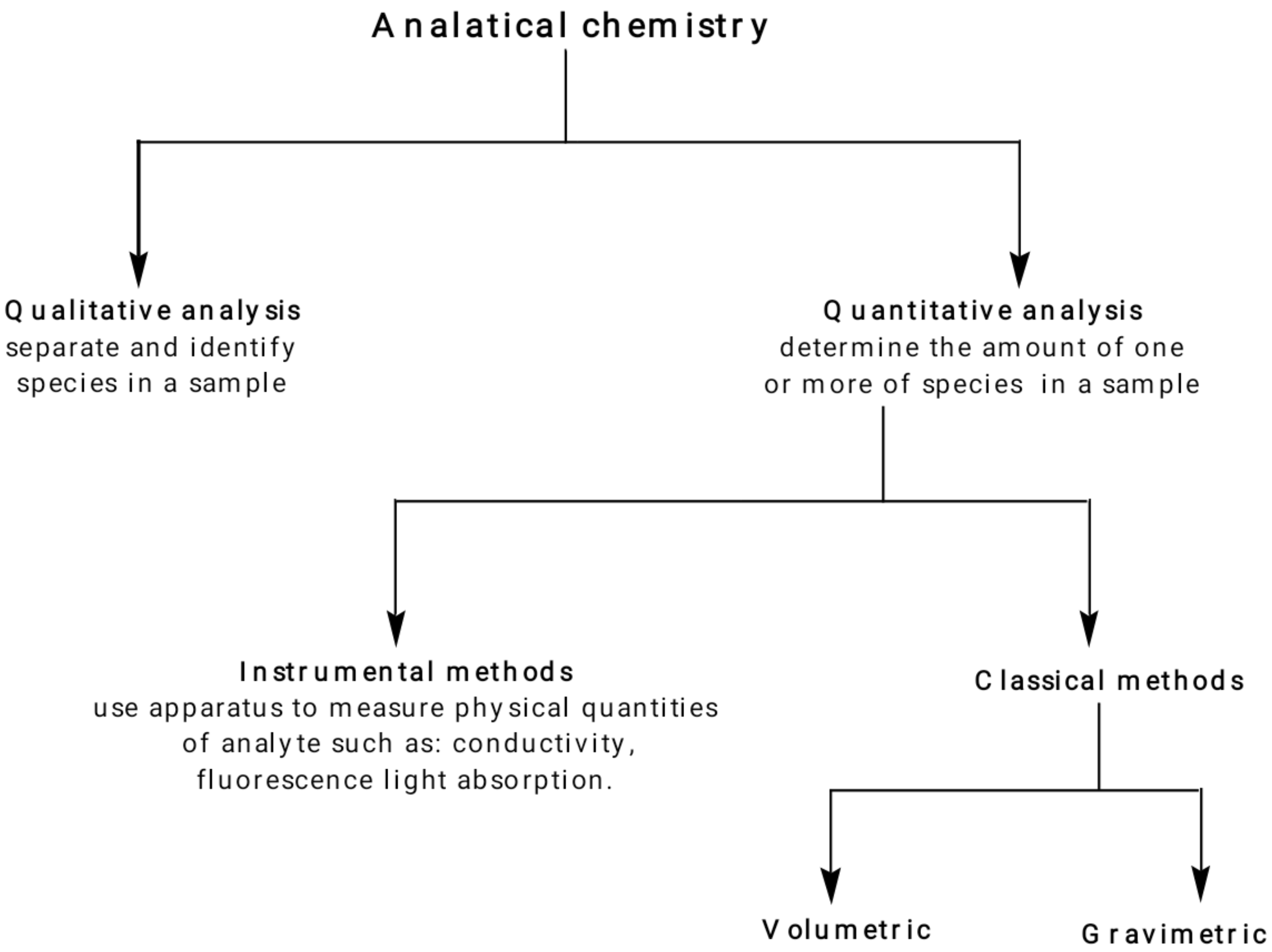
Quantitative analysis: Measuring the amount of analysis in the sample.

Analysis: Qualitative and quantitative characteristics of chemical analytes.

Analytes: Components of a sample that are to be determined.

Abbreviations:

ph. ph.	Phenolphthaline indicator
M	Molarity
N	Normality
L. P.	Litmus paper
Conc.	Concentrated
Dil.	Diluted
D. W.	Distilled water
B. P.	Boiling point
Res.	Residue
Ac.	Acetate
Sat.	Saturated



Qualitative analysis:

Involves the identification of the constituents of materials by systematic methods. The materials are restricted to ordinary inorganic substances, the components of which may be detected by means of cation and anion analysis.

Apparatus and glassware used in qualitative

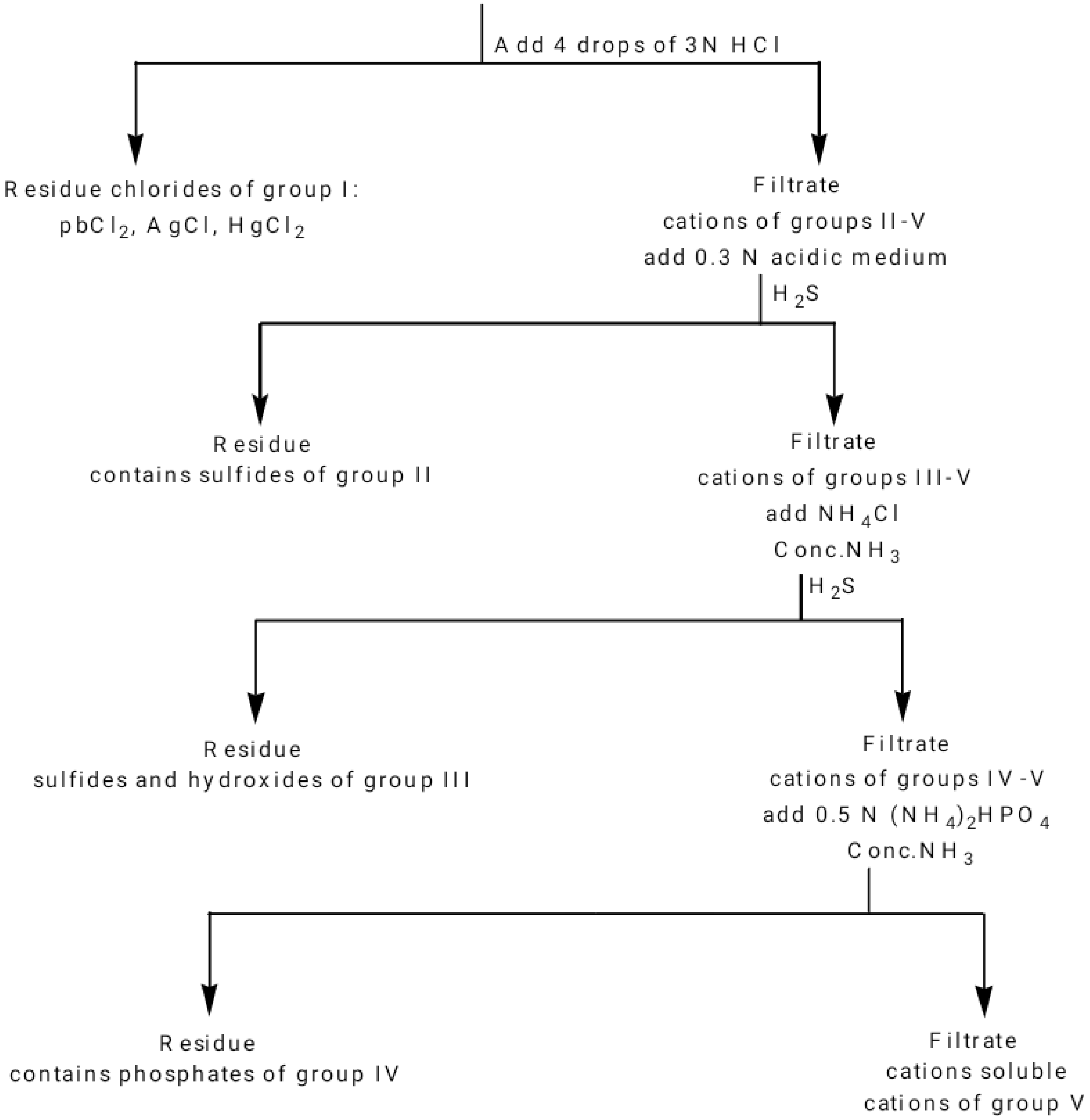
analysis:

1. Test tube.
2. Centrifuge test tube.
3. Centrifuge
4. Glass rod
5. water bath
6. Dropper.
7. Reagent bottle.
8. Washing bottle.
9. Rack.
10. Brush
11. Funnel
12. Measuring cylinder

Systematic separation of cations into groups:

The systematic analysis of the common cations is based upon the precipitation of groups of ions, so that the total number of ions can be broken into a small number of groups. After the group separation is made, the ions within the group must be separated to the extent necessary for individual identification.

Systematic separation of cations into groups



Analysis of group I cations (Ag^+, Pb^{2+}, Hg_2^{2+}):

Principle:

Group I can be separated from the other groups, since they form slightly soluble chlorides with the addition of hydrochloric acid. The other groups will remain in solution thus allowing the group I chloride precipitates to be removed and further tested.

Procedure:

Place 1 mL (10 drops) of the solution to be analyzed (mixture solution) in a test tube and add 4 drops of 3N HCl. Mix thoroughly and centrifuge then reject the filtrate.

To the residue add 5 drops of aqua regia*, then heat in a water bath for 5 minutes**, dillute with 1 mL of distilled water, heat in a water bath for 3 minutes*** and centrifuge.

Residue (silver chloride):

Add 10 drops of 3N ammonia, stir thoroughly, heat in a water bath to dissolve the residue and add 2 drops of phenolphthaline (ph.ph.) then add 3N HCl drop by drop till changing color from pink to colorless, note forming of white precipitate indicates presence of silver ions.

Filtrate:

Contain Hg_2^{2+} and Pb^{2+} ions: devide the solution by hand into two equal parts one to detect mercurous ions and the other to detect lead ions.

1. Detection of Hg_2^{2+} ions:

   Add 1 drop of conc. ammonia, 1 drop of 1N KI and 5 drops of 4N NaOH, formation of brown residue indicates the presence of mercurous ions.

2. Detection of Pb^{2+} ions:

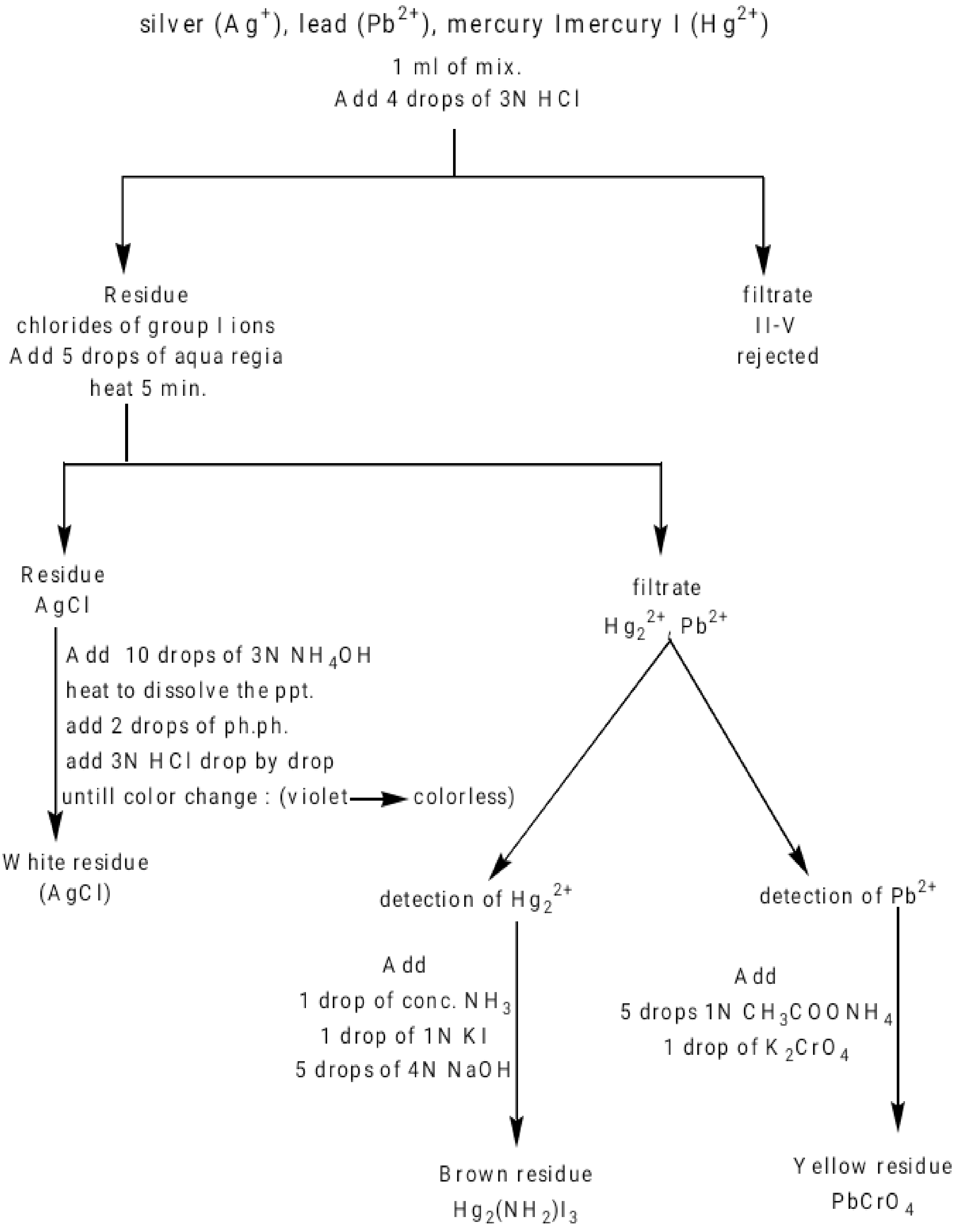
Add 5 drops of 1N CH_3COONH_4 and 1 drop of 1N K_2CrO_4. Yellow precipitate confirms presence of lead ions.

* Aqua regia prepared by mixing 3 volumes of concentrated HCl with 1 volume of concentrated HNO_3.

** To dissolve Hg_2Cl_2 by oxidizing with aqua regia.

*** Dillution and heating to dissolve $PbCl_2$.

Systematic separation and detection of group I cations



Chemical Reactions Involved in the Separation of Group I Cations:

(Group precipitation):

Lead, silver and mercurous ions give white precipitate with the chloride ion in an acid solution:

$$Pb^{2+} + 2Cl^{-} \rightleftharpoons PbCl_2$$

$$Ag^{+} + 2Cl^{-} \rightleftharpoons AgCl$$

$$Hg^{2+} + 2Cl^{-} \rightleftharpoons Hg_2Cl_2$$

Confirmation of presence of silver ion:

$$AgCl + 2NH_3 \rightleftharpoons Ag(NH_3)_2^{+} + Cl$$

$$Ag(NH_3)_2^{+} + Cl + 2H_3O^{+} \rightleftharpoons AgCl + 2NH_4 + 2H_2O$$

Confirmation of presence of mercury I ion:

$$Hg_2Cl_2 + HOCl + H_3O^{+} + Cl^{-} \rightleftharpoons 2[HgCl_4]^{2-} + 2H_2O$$

$$2[HgCl_4]^{2-} + 2NH_4^{+} + 3I^{-} \rightleftharpoons Hg_2(NH_2)I_3 + 8Cl^{-} + H_2O$$

Confirmation of presence of lead ion:

$$Pb^{2+} + CrO_4^{2-} \rightleftharpoons PbCrO_4$$

Analysis of group II cations

Mercury (Hg^{2+}), copper (Cu^{2+}), bismuth (Bi^{3+}), lead (Pb^{2+}), cadmium (Cd^{2+}), tin I (Sn^{2+}), tin II (Sn^{4+}), arsenic I (As^{3+}), arsenic II (As^{5+}), antimony (Sb^{3+}).

Principle:

Group II are readily separated from the other groups by adding H_2S to the solution after the group I cations have been removed and adjusting the pH to 0.5 (0.3N). We can remove the cations of group II as sulfides precipitate.

Procedure:

Place 1 mL (10 drops) of the solution to be analyzed (mixture solution) in a test tube and add 2 drops of methyl violet. Make barely alkaline with concentrated ammonia (use litmus paper), then add concentrated HCl (use litmus paper) until it just acid (the colour changed from violet to green and pH of the medium becomes 0.5*[0.3 N]. Add 10 drops of thioacetamide solution and heat in a boiling water bath for 5 min.**. Centrifuge and reject filtrate.

Precipitate: consists of sulfides of cations of group II (As_2S_3, As_2S_5, Sb_2S_3, SnS, SnS_2, HgS, PbS, CuS, Bi_2S_3, CdS).

Separation of group IIA and IIB:

Add 8 drops of 3N KOH to the residue, stir and heat in water bath for 3 min. centrifuge.

Residue: consist of sulfides of group IIA: HgS, CuS, CdS, PbS, Bi_2S_3.

Filtrate : is solution of soluble complex ions of group IIB cations, which are arsenic, antimony and tin.

* The directions for acidifying the solution, produce a solution which is 0.3 N. this is the correct acidify for the separation of group II. If the solution is too acid, the precipitation of some of the cations may be incomplete. If the solution is not sufficiently acid, some of the cations of group III cations may be precipitated as sulfides such as zinc and cobalt.

** Heating is get rid of excess of H_2S. If the H_2S is not expelled from the centrifugate, atmospheric oxidation will convert S^{2-} to SO_4^{2-}. The presence of sulfate will cause a partial precipitation of group IV cations as sulfates (such as barium sulfate).

Analysis of group IIA cations:

Procedure:

To the residue from subgroup separation, add 10 drops of 3N HNO_3, heat in a water bath for 2 min. and centrifuge.

Residue : (HgS)

Dissolve in 4 drops of aqua regia. Add 10 drops of distilled water and boil in a water bath for 2 min. Cool and add 2 drops of $SnCl_2$ solution. White or gray precipitate of Hg and Hg_2Cl_2 confirms presence of mercuric ion.

Filtrate: contains lead, bismuth, copper and cadimium ions. Add concentrated ammonia drop by drop to make barely alkaline (use litmus paper) then centrifuge.

Residue : $Bi(OH)_3$

Add 10 or more drops of freshly prepared potassium stannite* solution. Black residue indicates presence of bismuth ion.

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* To prepare potassium stannite solution, add 3N KOH drop by drop to 2 drops of stannous chloride solution until the gelatinous precipitate of stannous hydroxide, first forms, barely dissolves.

$$Sn^{2+} + 2OH^{-} \rightleftharpoons \underset{\text{gelatinous}}{Sn(OH)}$$

$$Sn(OH)_2 + OH^{-} \rightleftharpoons \underset{\text{Soluble}}{Sn(OH)_3^{-}}$$

Filtrate: contains soluble copper and cadmium complex ions. Deep blue solution confirms presence of copper ion. To test for cadmium ion, add 5 drops of thioacetamide solution and place in boiling water bath* for 5 min. Yellow precipitate indicates presence of cadmium ion.

Analysis of group IIB cations:

Procedure:

To filtrate from subgroup separation, add 10 drops of concentrated HCl, stir and heat in a water bath for 1 min.*centrifuge.

Residue: (As_2S_3, As_2S_5)

Add 4 drops of conc. HNO_3, heat in water bath for 5 min. Add 5 drops of 0.5 N $AgNO_3$ solution, stir, then add 15 drops of 2.5 N NaAc solution. Formation of reddish – brown precipitate confirms presence of arsenic.

Filtrate: contains antimony and stannous ions. Divide into two unequal portions.

* The solution is heated to expel H_2S, with prevent the antimony and tin ions precipitating.

Small portion: (Make a test for antimony)

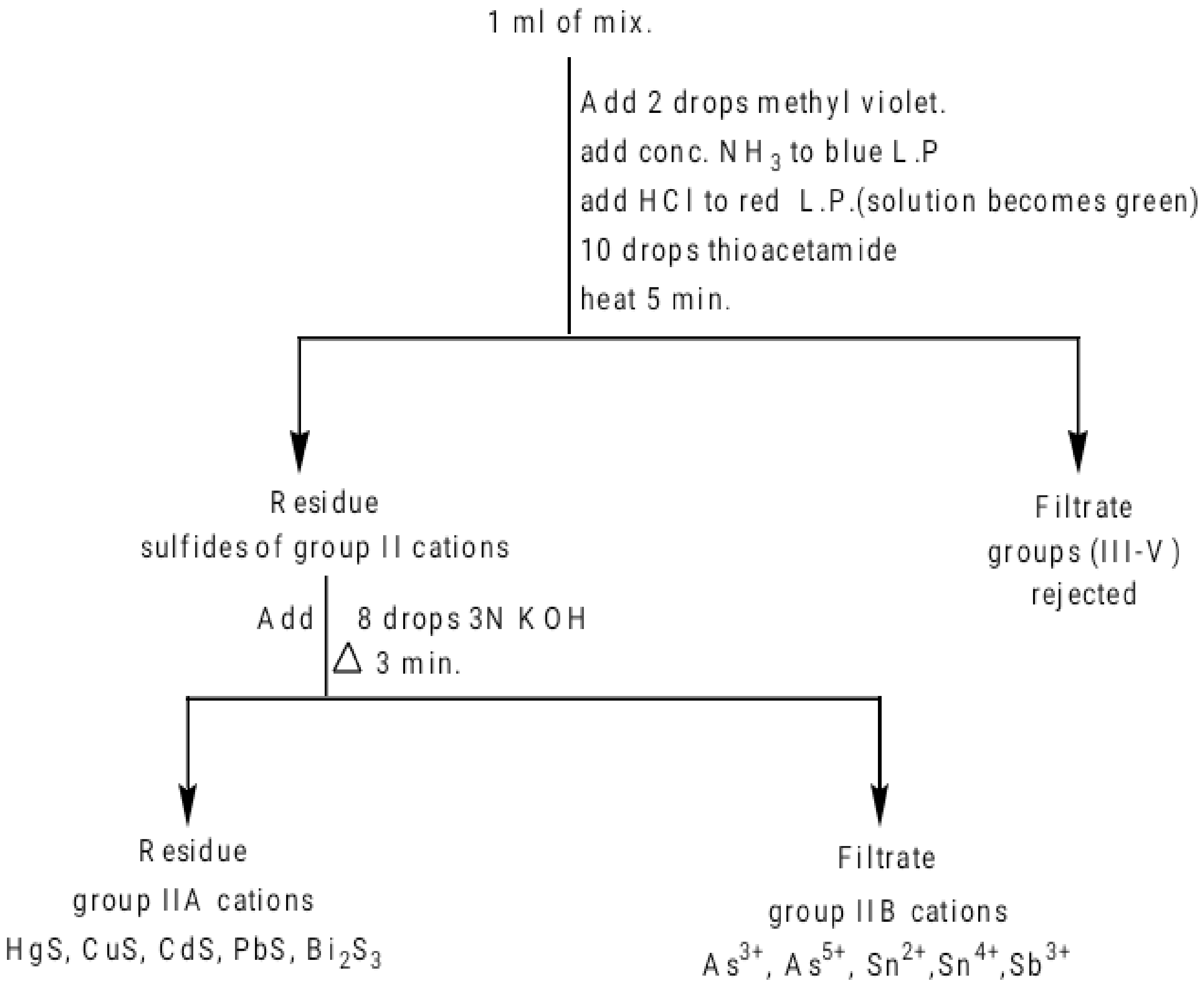
Add conc. NH_3 drop by drop (use litmus paper) then add 0.3 g oxalic acid, add 3 drops of thioacetamide. Formation of orange precipitate indicates presence of antimony.

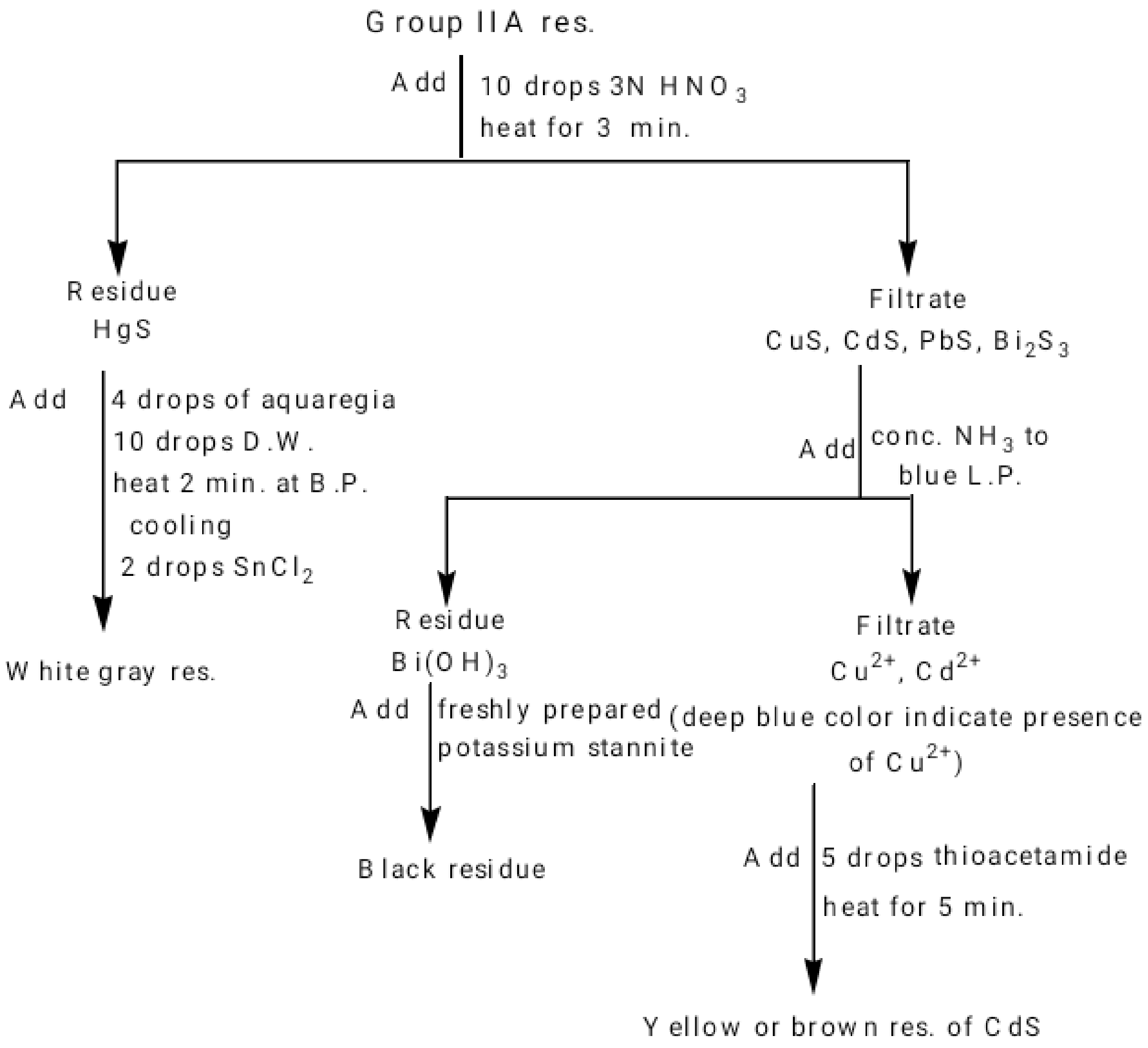
Large portion: (Test for tin). Add an equal volume of 3N HCl to this portion. Place a piece of Mg* ribbon. 2 cm long in the solution and allow to stand until completely dissolve. Add 4 drops of saturated $HgCl_2$ solution. White or gray precipitate confirms presence of tin.

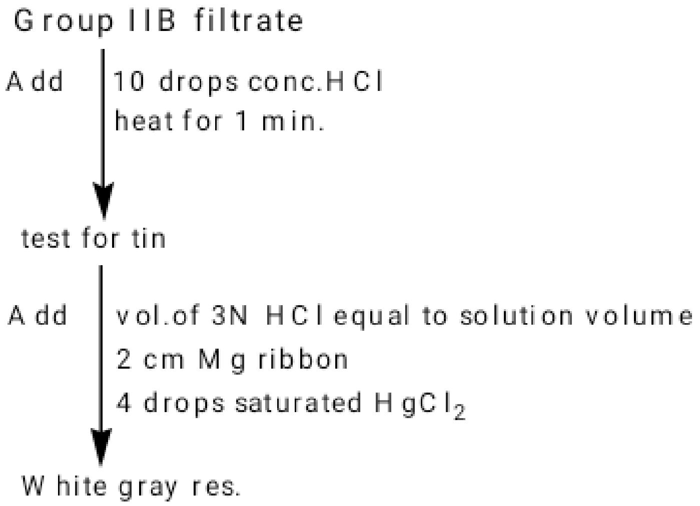
* The magnesium metal is added to reduce the antimony ions completely to the metal, and stannic to stannous ions.

Systematic separation and detection of group II cations

Detection of group II



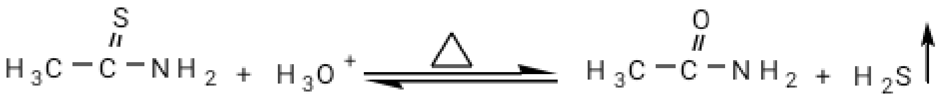




Chemical Reactions Involved in Separation and

Identification of group II cations:

Note: Thioacetamide in aqua acid medium evolve H_2S which precipitate group II cations.



$$H_3C-C(=S)-NH_2 + H_3O^+ \overset{\Delta}{\rightleftharpoons} H_3C-C(=O)-NH_2 + H_2S\uparrow$$

Thioacetamide

Copper ion precipitate as black CuS with hydrogen sulfide:

$$Cu^{2+} + H_2S + 2H_2O \rightleftharpoons CuS + 2H_3O^+$$

Bismuth ions precipitate as dark brown Bi_2S_3 with hydrogen sulfide:

$$2Bi^{3+} + 3H_2S + 6H_2O \rightleftharpoons Bi_2S_3 + 6H_3O^+$$

Lead ions give a black precipitate of PbS with hydrogen sulfide:

$$Pb^{2+} + H_2S + 2H_2O \rightleftharpoons PbS + 2H_3O^+$$

Cadmium ions precipitate as orange - red CdS with hydrogen sulfide:

$$Cd^{2+} + H_2S + 2H_2O \rightleftharpoons CdS + 2H_3O^+$$

Arsenic I and arsenic II ions give yellow precipitate with hydrogen sulfide:

$$2H_3AsO_3 + 3H_2S \rightleftharpoons As_2S_3 + 6H_2O$$

$$2H_3AsO_4^- + 5H_2S + 2H_3O^+ \rightleftharpoons As_2S_5 + 10H_2O$$

Antimon ions give orange precipitate with hydrogen sulfide:

$$2SbCl_4^- + 3H_2S + 6H_2O \rightleftharpoons Sb_2S_3 + 6H_3O + 8Cl^-$$

Stannous ions produce a brown precipitate of SnS with H_2S:

$$Sn^{2+} + H_2S + 2H_2O \rightleftharpoons SnS + 2H_3O^+$$

Stannic ions produce a light yellow precipitate of SnS2 with H2S:

$$SnCl_6^{2-} + 2H_2S + 4H_2O \rightleftharpoons SnS_2 + 4H_3O^+ + 6Cl^-$$

Detection of mercury II ion:

$$2HgCl_4^{2-} + SnCl_4^{2-} \rightleftharpoons Hg_2Cl_2 + SnCl_6^{2-} + 4Cl^-$$

Detection of bismuth ion:

$$2Bi(OH)_3 + 3Sn(OH)_3 + 3OH^- \rightleftharpoons 2Bi + 3Sn(OH)_6^{2-}$$

Detection of stannous and stannic ions:

$$SnCl_6^{2-} + Mg \rightleftharpoons SnCl_4^{3-} + 2Mg^{2+} + 2Cl^-$$

$$2SnCl_6^{3-} + 3Mg \rightleftharpoons 2Sn + 3Mg^{2+} + 12Cl^-$$

$$SnCl_4^{2-} + 2HgCl_2 \rightleftharpoons Hg_2Cl_2 + SnCl_6^{2-}$$

$$2HgCl_2 + SnCl_4^{2-} \rightleftharpoons 2Hg + SnCl_6^{2-}$$

Analysis of group III cations: Aluminium (Al^{3+}), Chromium (Cr^{3+}), Zinc (Zn^{2+}),Ferrous (Fe^{2+}), Manganese (Mn^{2+}), Cobalt (Co^{2+}) ,Nickel (Ni^{2+})

Procedure:

The cationsof group III don't form slightly soluble chlorides and don't form sulfides through precipitation by H_2S at pH 0.5. some sulfides, however that are not precipitate by H_2S in acidic media will be precipitate by H_2S when the acidity is lowered or base is added before treatment, to get a sulfides and hydroxides of cations.

Procedure:

Place 1 ml of the solution to be analyzed (mixture) in a test tube, add 4 drops of saturated NH_4Cl, then add conc. ammonia drop by drop until solution is distinctly alkaline (use l. p.) to ensure complete precipitation of group III cations. Add 10 drops of thioacetamide solution and place in boiling water bath for 5 min. then centrifuge, reject the filtrate. precipitate contains sulfides and hydroxides of group III.

Separation of group III into subgroups:

Add 5 drops of aqua regia to the residue, stir and make solution basic with conc. KOH (use l. p.), then add 2ml of

H_2O_2*slowly with stiring, heat in a water bath for 3 min. and centrifuge.

* H_2O_2 is added to oxidizing chromite to chromate ion. At the same time, ferrous and cobaltous hydroxides to ferric and cobaltic hydroxides. Manganous hydroxide is oxidized to hydrated manganese.

Note: A large excess of H_2O_2 is to be avoided, since the hydroxides of iron, cobalt and nickel may be interfere in a strong basic solution with the test for aluminium and zinc ions.

Analysis of group IIIA cations: (Al^{3+}, Zn^{2+}, Cr^{3+})

Procedure:

To the filtrate add 10 drops of saturated NH_4Ac, acidify the solution with 3N HAc (use l. p.). Now add 3N ammonia until solution is ammoniacal*. Centrifuge.

Residue: ($Al(OH)_3$)

Add 3 drops of 3N HCl drop by drop until residue is dissolved. Add 3 drops of saturated NH_4Ac and 3 drops of aluminon**, then make decidedly ammoniacal with 3N NH_3. Allow mixture to stand 2 min. the centrifuge. Separation of a red precipitate confirms presence of aluminium ion.

Filtrate: contains Cr^{3+}, Zn^{2+}***

Add 1N $Ba(Ac)_2$ until precipitation is complete. Centrifuge.

Residue: contains $BaCrO_4$

Add 3N HAc, drop by drop until acid (use litmus paper), then add 1 drop of $Pb(Ac)_2$. Formation of yellow precipitation indicates presence of chromium ion.

Filtrate: contains Zn^{2+}

Acidify the solution with 3N HAc (use litmus paper), add 5 drops of thioacetamide solution and place in boiling water bath for 5 min. Formation of a white precipitate confirms presence of zinc ion.

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* The precipitation of aluminium hydroxide is complete in the buffered ammonia – ammonium acetate solution.

** Aluminon dye form a red lake with $Al(OH)_3$. This test is specific for aluminium .

*** The solution must be yellow if chromium is present.

Analysis of group IIIB cations: (Fe^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+})

Procedure:

Dissolve a precipitate in conc. HCl. Dilute resulting solution to approximately 2 mL and divide it into four portions.

First portion (test for Mn^{2+})

Add 0.2 g of solid sodium bismuthate ($NiBiO_3$). Stir well, then centrifuge. Reddish – purple* color in the liquid confirms presence of manganese ion.

Second portion (test for Fe^{2+})

Add 2 drops of 3N NH_4CNS. Appearance of deep ** red color confirms presence of ferric ion.

Third portion (test for Co^{2+})

Add solid NaF*** with stirring, until undissolved NaF remains. Let 10 drops of alcoholic NH_4CNS run down side of test tube containing this portion. Appearance of blue – green color at junction of the two liquids confirms presence of cobalt ion.

Fourth portion (test for Ni^{2+})

Add solid NaF*** with stirring, until undissolved NaF remains. Make the solution basic with 3N NH_3, then add 4 drops of DMG (dimethylglyoxime). Formation of a red precipitate confirms presence of nickel ion.

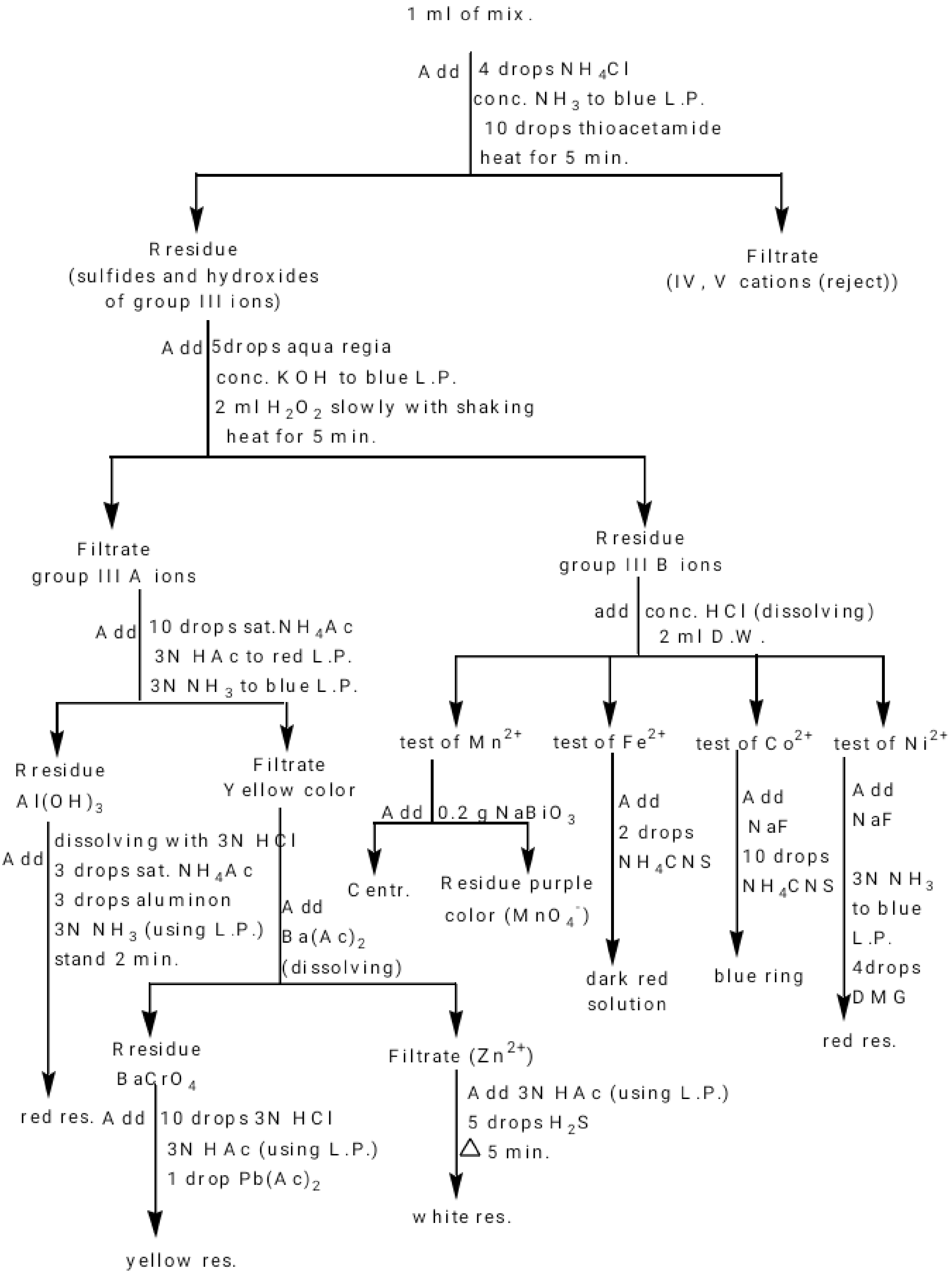
* In an acid solution, sodium bismuthate, oxidizes manganous ions to the purple – colored permanganate ions.

$$2\,Mn^{2+} + 5BiO_3^- + 14\,H_3O^+ \longrightarrow \underset{\text{Purple}}{2\,MnO_4^-} + 5Bi^{3+} + 21\,H_2O$$

** The color must be dark reddish – brown. Traces of ferric ions from the reagent give a pale red color in this sensitive test.

** If sodium floride added to a solution containing ferric, cobalt and nickel ions, the interference from ferric ion in the tests for cobalt and nickel is eliminated.

Detection of group III cations



Chemical reactions involved in the separation and identification of group III cations

$$Al^{3+} + 3NH_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3NH_4^+$$

$$Fe^{3+} + 3NH_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3NH_4^+$$

$$Cr^{3+} + 3NH_3 + 3H_2O \rightleftharpoons Cr(OH)_3 + 3NH_4^+$$

$$Ni^{2+} + 6NH_3 \rightleftharpoons Ni(NH_3)_6^{2+}$$

$$Co^{2+} + 6NH_3 \rightleftharpoons Co(NH_3)_6^{2+}$$

$$Zn^{2+} + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{2+}$$

$$Fe(OH)^3 + 3S^{2-} + 6NH^{4+} \rightleftharpoons \underset{\text{black}}{FeS_3} + 6NH_3 + 6H_2O$$

$$Mn^{2+} + S^{2-} \rightleftharpoons \underset{\text{pink}}{MnS}$$

$$Ni(NH_3)_6^{2+} + S^{2-} \rightleftharpoons \underset{\text{black}}{NiS} + 6NH_3$$

$$Co(NH_3)_6^{2+} + S^{2-} \rightleftharpoons \underset{\text{black}}{CoS} + 6NH_3$$

$$Zn(NH_3)_6^{2+} + S^{2-} \rightleftharpoons \underset{\text{white}}{ZnS} + 6NH_3$$

Detection of aluminium ion:

$$Al(OH)_4^- + CH_3COOH \rightleftharpoons Al^{3+} + 4CH_3COO^- + 4H_2O$$

$$Al^{3+} + 3NH_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3NH_4^+$$

Detection of chromium ion:

$$Ba^{2+} + CrO_4^{2-} \rightleftharpoons BaCrO_4$$

Detection of zinc ion:

$$Zn(NH_3)_4^{2+} + 4CH_3COOH \rightleftharpoons Zn^{2+} + 4NH_4 + 4CH_3COO^-$$

$$Zn^{2+} + H_2S + 2H_2O \rightleftharpoons ZnS + 2H_3O^+$$

Detection of manganese ion:

$$MnO(OH)_2 + 4H_3O^+ + 2Cl^- \rightleftharpoons Mn^{2+} + Cl_2 + 7H_2O$$

$$Mn^{2+} + 5BiO_3^- + 14H_3O^+ \rightleftharpoons 2MnO_4^- + 5Bi^{3+} + 21H_2O$$

Detection of ferric ion:

$$Fe(OH)_3 + 3H_3O^+ \rightleftharpoons Fe^{3+} + 6H_2O$$

$$Fe^{3+} + 6CNS^- \rightleftharpoons Fe(CNS)_6^{3-}$$

Ferric interfere with tests of cobalt and nickel, this interference is prevented as follow:

$$Fe^{3+} + 6F^- \rightleftharpoons FeF_6^{3-}$$

Detection of cobalt ion:

$$2Co(OH)_3 + 6H_3O^+ + 2Cl^- \rightleftharpoons 2Co^{2+} + Cl2 + 12H_2O$$

$$2Co^{2+} + 4CNS^- \rightleftharpoons Co(CNS)_4^{2-}$$

Detection of nickel ion:

$$Ni(OH)_2 + 2H_3O^+ \rightleftharpoons Ni^{2+} + 4H_2O$$

$$Ni^{2+} + 2NH_3 + 2C_2H_8O_2N_2 \rightleftharpoons (C_2H_8O_2N_2)_2Ni + 2NH_4^+$$

Analysis of group IV cations: Magnesium (Mg^{2+}),Strontium (Sr^{2+}), Calcium (Ca^{2+}), Barium (Ba^{2+})

Principle:

Group IV and V will remain in a solution after the groups I, II, and III have been removed because their chlorides, sulfides, and hydroxides are soluble enough after the other group precipitation conditions.

Group IV cations form insoluble carbonates, this principle is used to separate them from group V cations, which form soluble carbonates.

Procedure:

Place 1 mL of the solution to be analyzed (mixture) in a test tube, add 10 drops of 0.5 N $(NH_4)_2HPO_4$ and concentrated ammonia until strongly ammoniacal (use l. p.), centrifuge.

Residue:

Contains phosphates of barium, calcium, strontium and magnesium. Treat a precipitate with 5 drops of concentrated* HAc and stir. Dilute the solution to 2 ml with distilled water, add 5 drops of 2N K_2CrO_4, and stir for 1 min. Centrifuge.

Residue:

Contains $BaCrO_4$, add 6 drops of conc. HCl and heat in a water bath until volume is reduced to one half**. Confirm presence of barium ion by flame test (yellow – green).

Filtrate:

Contains strontium, calcium, and magnesium ions. Make solution strongly basic with ammonia (use litmus paper) and centrifuge then reject the filtrate (contains chromate ions). Dissolve the residue in 5 drops of conc. HAc, dilute with 5 drops of distilled water. Add 5 drops of 2N $(NH_4)_2SO_4$, heat to boiling in water bath, cool and centrifuge.

Residue:

Contains $SrSO_4$, add 3 drops of conc. HCl. Confirm presence of strontium ion by flame test (crimson – red).

* To dissolve barium chromate which precipitate in diluted acetic acid.

** Barium chromate is not sufficiently volatile to give a flame test, consequently, this compound must be converted to one which volatile by evaporation with conc. HCl and converted to $BaCl_2$ which give excellent flame test.

Filtrate:

Contains calcium and magnesium ions. Add 5 drops of $(NH_4)_2C_2O_4$ and heat to boiling in water bath. White precipitate or clouding of solution indicates presence of calcium ion. Centrifuge.

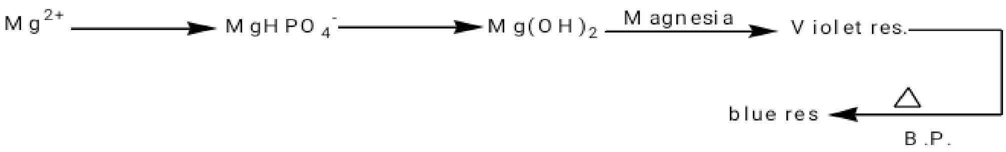
Residue:

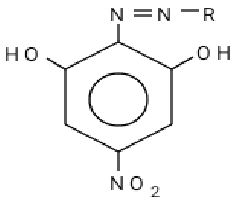
Contains CaC_2O_4. Add 2 drops of conc. HCl confirm the presence of calcium ion by flame test (brick – red).

Filtrate:

Contains magnesium ions. Add 2 drops of p-nitro benzo azo resorcinol (magnesia*) and 3 drops of conc. KOH. Heat in water bath for 5 min. then centrifuge. Formation of a blue precipitate confirms presence of magnesium ion.

* Magnesia is specific dye for magnesium ion in the presence of other cations and is used as a confirmatory test for the magnesium ion.





p-Nitro benzo azo resorcinol

Note:

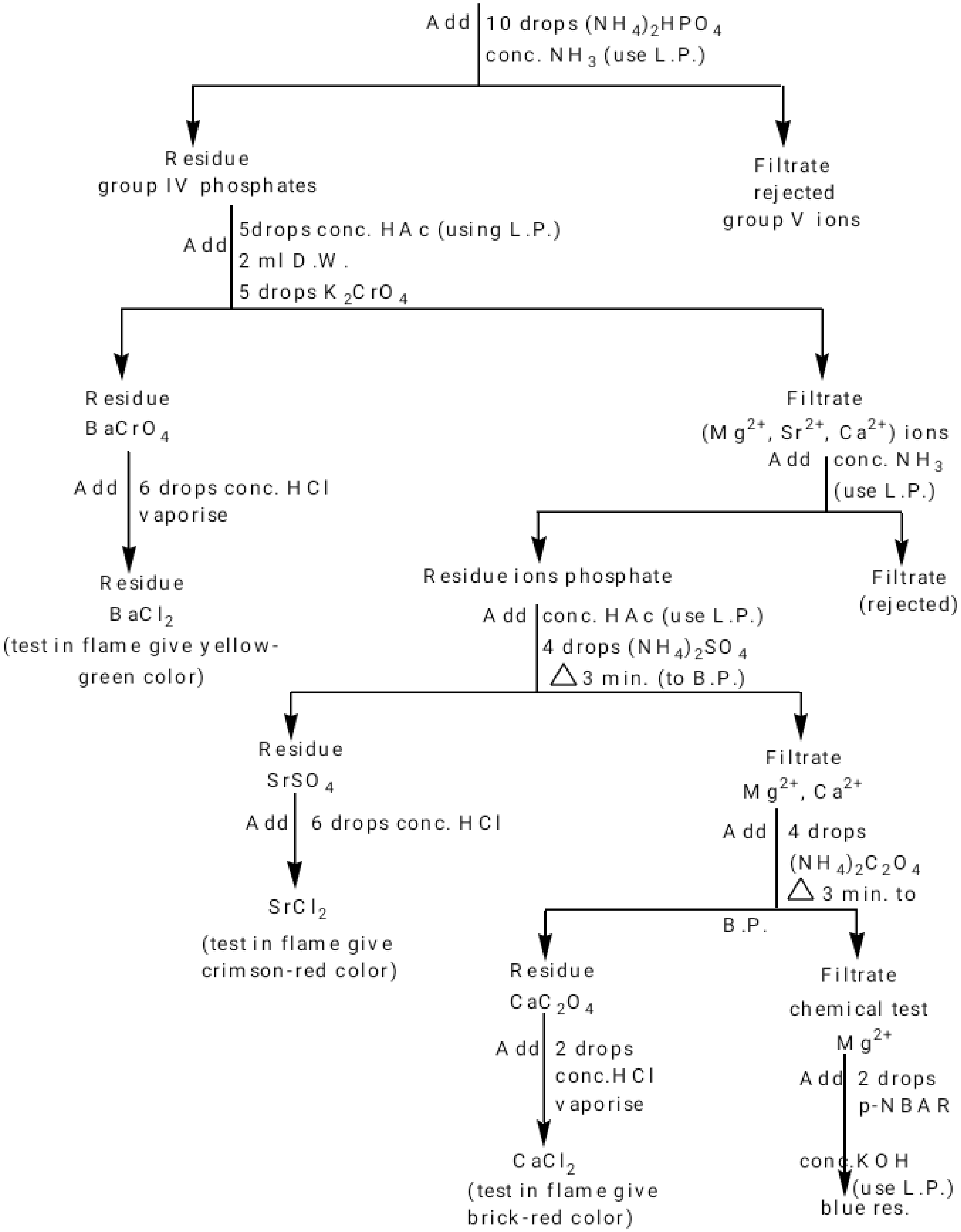
1. In test Ca^{2+}, Sr^{2+} and Ba^{2+} in flame test, must use their chloride salt. (Why?).
2. We can't do flame test for magnesium ion, so tested chemically.

Detection of group IV cations

Group III cations: Mg^{2+}, Sr^{2+}, Ca^{2+}, Ba^{2+}.

Reagent: carbonate or phosphate ion in alkaline medium.

1 ml of mix.



Chemical reactions involved in the separation and identification of group IV cations:

$$3Ba^{2+} + 2HPO_4^{2-} + 2NH_3 \rightleftharpoons Ba_3(PO_4)_2 + 2NH_4^+$$

$$3Sr^{2+} + 2HPO_4^{2-} + 2NH_3 \rightleftharpoons Sr_3(PO_4)_2 + 2NH_4^+$$

$$3Ca^{2+} + 2HPO_4^{2-} + 2NH_3 \rightleftharpoons Ca_3(PO_4)_2 + 2NH_4^+$$

$$3Mg^{2+} + 2HPO_4^{2-} + 2NH_3 + 2H_2O \rightleftharpoons MgNH_4PO_4.6H_2O$$

$$\begin{array}{lcll}
Ba_3(PO_4)_2 & & \rightleftharpoons & 3Ba^{2+} \\
Sr_3(PO_4)_2 & & \rightleftharpoons & 3Sr^{2+} \\
 & + 4CH_3COOH & & \\
Ca_3(PO_4)_2 & & \rightleftharpoons & 3Ca^{2+} \\
MgNH_4PO_4.6H_2O & & \rightleftharpoons & Mg^{2+}
\end{array}$$

Detection of barium ion:

$$Ba^{2+} + CrO_4^{2-} \rightleftharpoons BaCrO_4$$

$$2BaCrO_4 + 16H_3O^+ + 6Cl^- \rightleftharpoons 2Ba^{2+} + 2Cr^{3+} + 3Cl_2 + 24H_3O^+$$

Detection of strontium ion:

$$Sr^{2+} + SO_4^{2-} \rightleftharpoons SrSO_4$$

Detection of calcium ion:

$$Ca^{2+} + C_2O_4^{2-} \rightleftharpoons CaC_2O_4$$

Detection of magnesium ion:

$$Mg^{2+} + 2OH^{-} \rightleftharpoons Mg(OH)_2$$

This precipitate has the property of adsorbing certain organic dyse to form colored lakes. This dye is magnesia.

Analysis of group V cations: Ammonium (NH_4^+), Potassium (K^+), Sodium (Na^+)

This group called soluble group and includes sodium, potassium and ammonium ions. The salts of these cations are quite soluble. This accounts for the fact that there is no precipitating agent for the group.

Identification of sodium and potassium ions:

Use chloride salts for Na^+ and K^+ and test in flame.

Na^+ give yellow color in flame.

K^+ give violet color in flame.

Identification of ammonium ion:

Place 5 drops of solution (may contain ammonia) is a small beaker and add 5 drops of water. Make solution alkaline with 3N KOH. Immediately cover beaker with a watch glass to which adheres a strip of moistened red litmus paper on convex side. Warm solution gently for 1 min. Even shading of litmus paper from red to blue confirms presence of ammonium ion.

Flame test:

The platinum wire to be used for the flame test must be free from any adhering substances which will color the Bunsen flame.

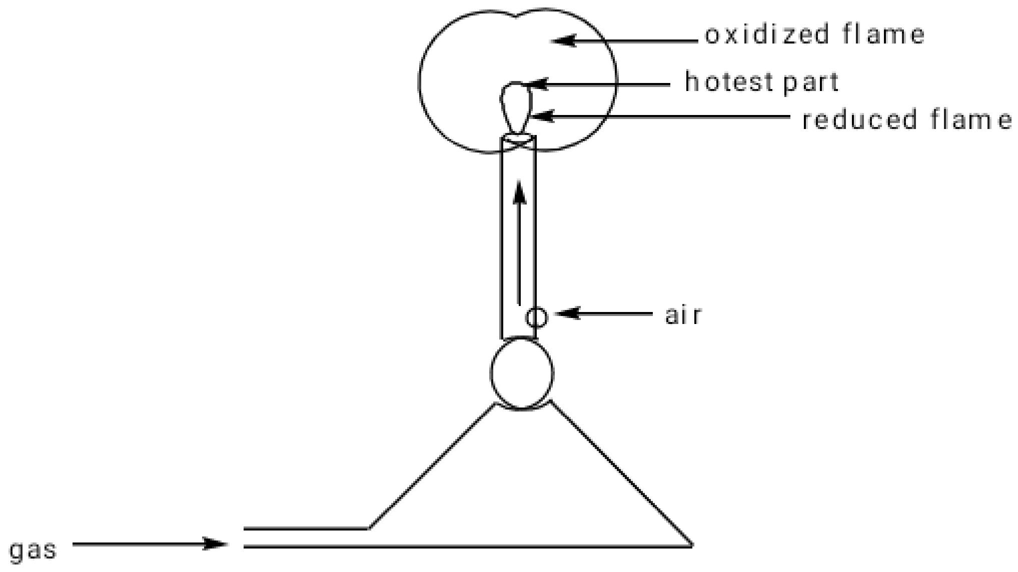
Cleaning platinum wire:

Dip the wire into clean, concentrated HCl, contained in a test tube, and then heat the wire in a flame until red – hot. If the flame is colored dip the wire again into the acid and heat in the flame again. Repeat this procedure until the wire imparts no appreciable color to the flame.

To make a flame test dip the loop of the clean platinum wire into the sample to be tested, and then insert the wire into the oxidizing portion of a colorless gas flame.

The table below show the flame colors of cations salts (especially chlorides), for group IV and V.

Cation	Flame color
Barium	Yellowish – green
Strontium	Crimson
Calcium	Brick - red
Sodium	Yellow
Potassium	Violet



Bunsen burner

Properties of platinum wire:

1. Does not dissolve in concentrated acids.
2. Does not fuse or melt.
3. Resists oxidation by atmosphere.
4. Does not react with the tested ions.

Systematic analysis of the anions:

The anions are negatively charged ions produced by the ionization of acids and salts. There is no specific classification for anions because:

1. Most anions composed of two or more elements bound in chemical combination.
2. Most anions give similar residues with cations. The present scheme identifies some commonly occurring anions. These

are as follows:

Borate	BO_2^-		
Bromide	Br-		
Carbonate	CO_3^{2-}	bicarbonate	HCO_3^-
Chloride	Cl^-	chlorate	ClO_3^-
Chromate	CrO_4^{2-}	perchlorate	ClO_4^-
Fluoride	F^-	chlorite	ClO_2^-
Iodide	I^-	hypochlorite	ClO^-
Nitrate	NO_3^-		
Nitrite	NO_2^-		
Oxalate	$C_2O_4^{2-}$		
Phosphate	PO_4^{3-}		
Sulfate	SO_4^{2-}		
Sulfide	S^{2-}		
Sulfite	SO_3^{2-}		
Thiocyanate	CNS^-		
Thiosulfate	$S_2O_3^{2-}$		
Acetate	CH_3COO^-		

Analysis of some anions

1. Sulfite ion SO_3^{2-}

Place 1 mL of sample to be tested into a test tube, add 2 drops of conc. HCl and 5 drops of $Ba(Ac)_2$. Centrifuge and discard any precipitate may formed. To clear centrifugate add 5 drops of H_2O_2. Formation of white precipitate confirms presence of sulfite.

2. Oxalate ion $C_2O_4^{2-}$

   Place 1 mL of sample to be tested into a test tube, add 10 drops of 1.5 N H_2SO_4. Heat with stirring in water bath for 1 min. Add 2 drops of 0.01 N $KMnO_4$ solution. Disappearance of pink color indicates presence of oxalate.

3. Sulfate ion SO_4^{2-}

   Place 1 mL of sample to be tested into a test tube, add IN $Ba(Ac)_2$ drop wise, until precipitation is complete. Centrifuge, and reject the filtrate. To the residue add 10 drops of 3N HCl. White residue confirms presence of sulfate.

4. Chromate ion CrO_4^{2-}

   Place 1 mL of sample to be tested into a test tube, add IN $Ba(Ac)_2$ drop wise, until precipitation is complete. Centrifuge, and reject the filtrate. To the residue, add 5 drops of 3N HCl, stir and centrifuge. To the filtrate, add 10 drops of 2.5N sodium acetate, yellow precipitate confirms presence of chromate.

5. Sulfide ion S^{2-}

   Take 0.5 g CdS in a small test tube, add 3 drops of 3N HCl cover mouth of the tube with a strip of filter paper moistened with 0.5 N $Pb(Ac)_2$. Brown or black coloration of test paper, caused by formation of PbS, indicates presence of sulfide.

6. Chloride ion Cl^-

   Place 1 mL of 1N HCl in a test tube, add 0.5 N $AgNO_3$, drop by drop, until white precipitate formed indicates presence of chloride.

$$Cl^- + Ag^+ \rightleftharpoons AgCl\downarrow$$

7. Nitrate ion NO_3^-

Place a small crystals of ferrous sulfate in a depression of aspot plate. Add 1 drop of the solution to be tested and 1 drop of concentrated H_2SO_4. Formation of a brown ring around the crystal indicates presence of nitrate ion.

$$3Fe(H_2O)_6^{2+} + NO_3^- + 4H_3O^+ \rightleftharpoons 3Fe(H_2O)_6^{3+} + NO + 6H_2O$$

$$Fe(H_2O)_6^{2+} + NO \rightleftharpoons Fe(H_2O)_5NO^{2+} + H_2O$$

General procedure for the experimentation and analysis of an unknown sample:

1. The unknown is a solution:

A- Physical examination:

1- Color of the solution:

Cupric ion is blue.

Nickelous ion is green.

Coblatous ion is pink (deep than manganous ion).

Manganous ion is pink.

2. Color of flame tests:

Volatile compound	Color of flame
Sodium	yellow
Potassium	violet
Calcium	brick - red
Strontium	crimson
Barium	yellow - green

B- Chemical examination:

1- Using litmus paper.

2- Cation analysis.

3- Anion analysis.

II- The unkown is a nonmetallic solid

A- Physical structure:

1- Crystal structure:

2- Color.

B- Solubility tests:

1- Water soluble

2- Soluble in acids

3- Insoluble in water and in acids.

III- The unknown is a metal

A- Physical examination.

B- Solubility tests.

C- Chemical examination.

References:

1- Quantitative inorganic analysis, Arthur Vogel, 2nd Ed.
2- Analytical Chemistry, Skoog.Holler.West, 8th. Ed.
3- Qualitative Analysis, Esmarch S.Gilreath. international student Edition, McGraw Hill.