Analytical Chemistry-1-Lab. for

First Stage of Chemistry

semester 2^{ed}

Laboratory Manual of Semimicro Qualitative Inorganic Analysis

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&
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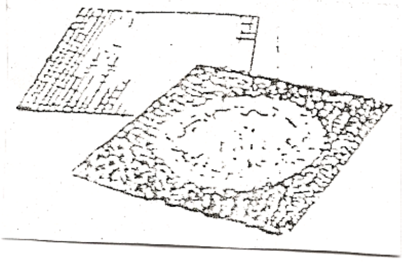

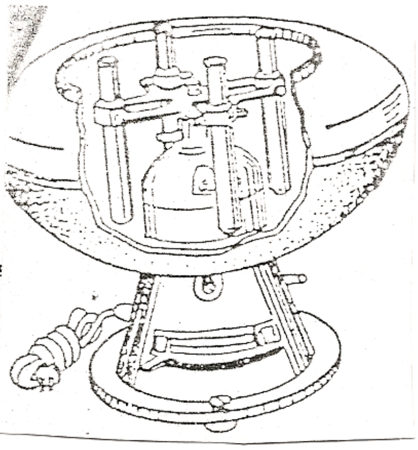

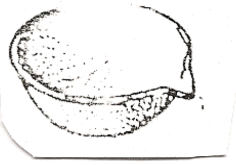

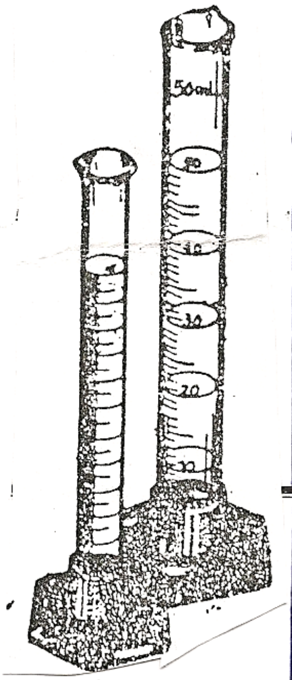
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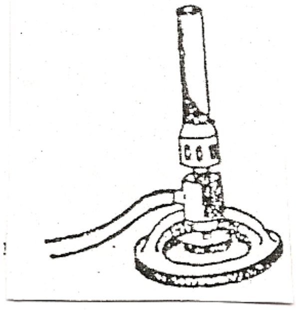

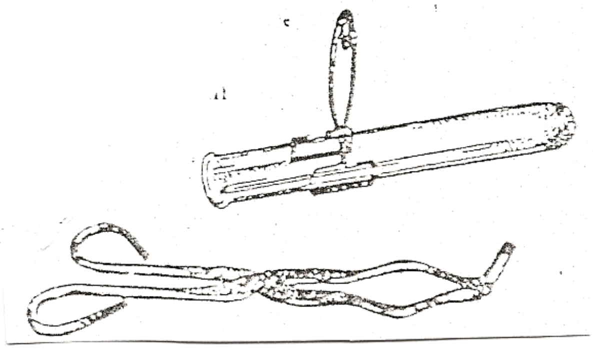

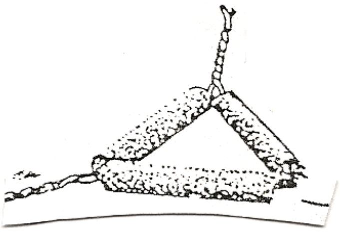

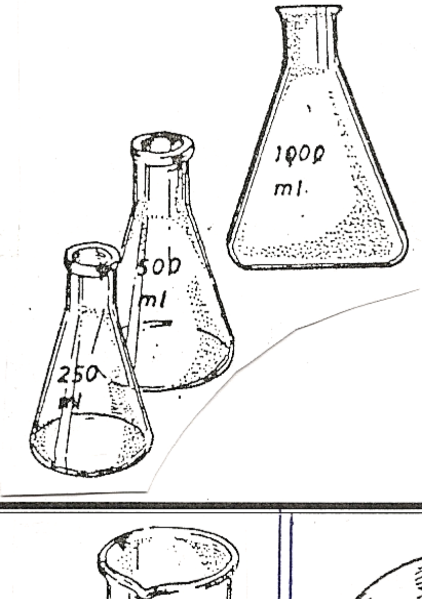
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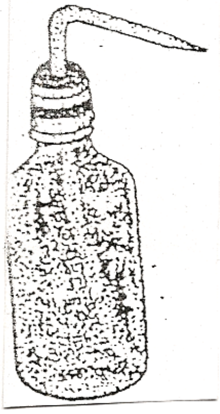

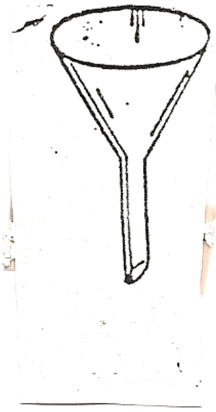

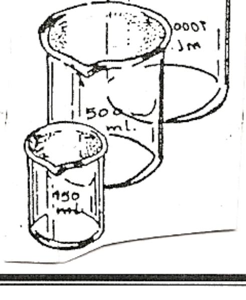
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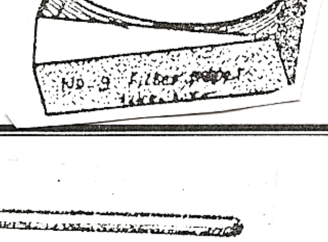
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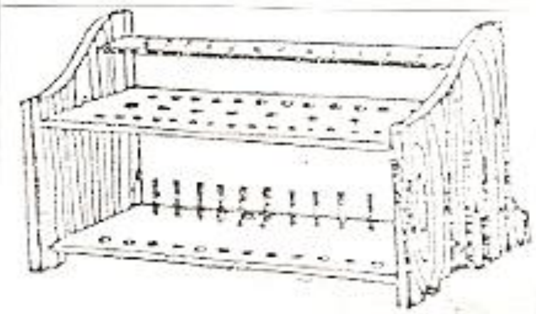
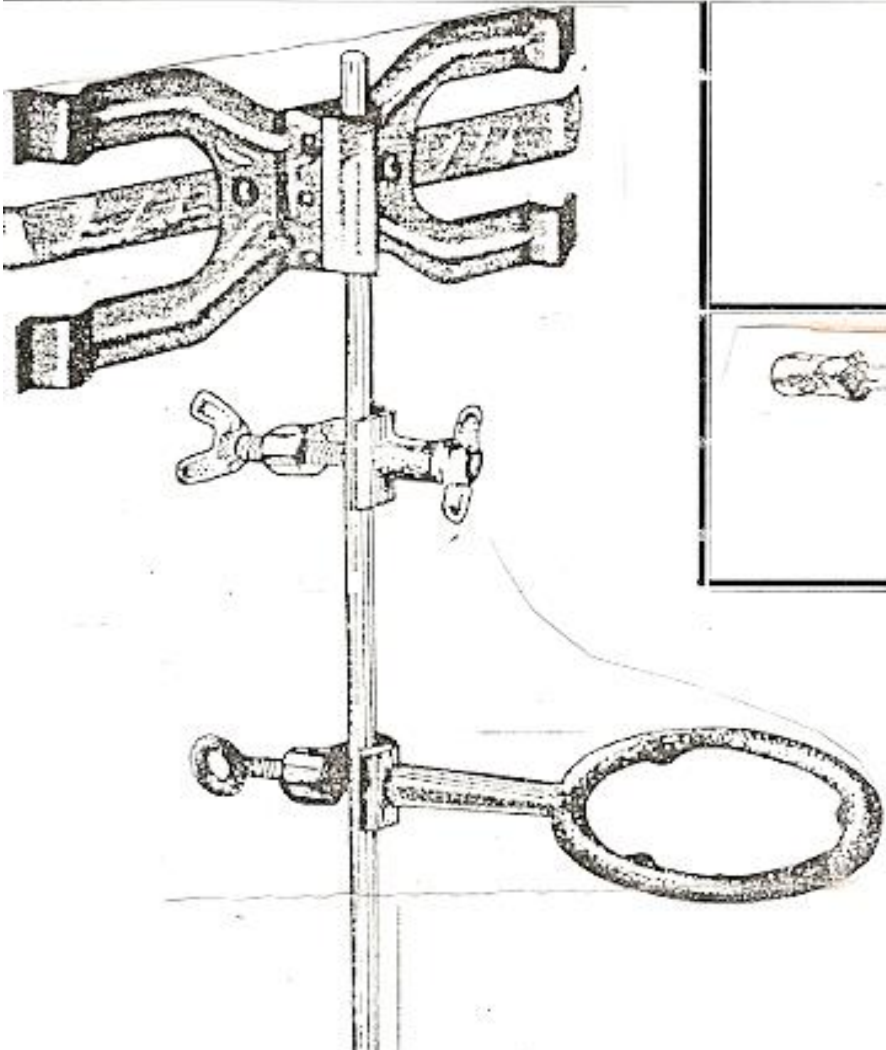
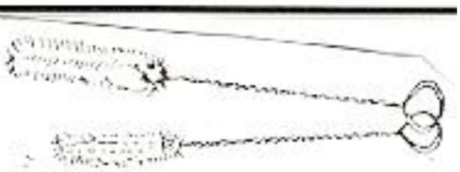






ارشادات مختبرية عامة

- لاخذ مادة صلبة من قنينة استعمل ملعقة زجاجية او بلاستيكية لا تسكب المادة الصلبة فوق ورقة الترشيح او انبوبة اختبار او دورق او كاس زجاجي بينما السوائل فقط هي التي تسكب في الاوعية الزجاجية المناسبة لها

- لا تغمر قطارة او ماصة في قنينة سائل او محلول لتستخدمه في سائل او محلول اخر

- لا تضع ابدا سداد قنينة او محلول فوق الرف او المنضدة تحاشيا من التلوث

- ضع جميع قناني المواد الكيميائية في الاماكن المخصصة لها بعد اخذك ما تحتاج منها دون حملها الى مكان عملك فالطلبة الاخرةن هم بحاجة لها ايضا

- لا تعيد الكمية الزائدة من المواد الكيميائية(الصلبة كانت ام سائلة الى قنينتها الاصلية) اعطها لزميل بحاجتها او اخبر احد مسؤولي المختبر لمعرفة ما يجب عمله للاستفادة منها

- لا تترك ابدا قنينة مواد كيميائيه مفتوحه فهناك كثير من المواد الكيميائيه التي يتغير تركيبها عند تعرضها للجو او ضوء الشمس او الضوءالاصطناعي اضافة الى احتمال تلوثها و تاكد من ان القنينه قد سدت باحكام عند اخذ جزء من المادة التي تحتويها

- ضع المواد الصلبة الزائدة التي لا يمكن الاستفادة منها واوراق الترشيح وبقايا عيدان الثقاب وغيرها قي وعاء المهملات ولا تضعها في الحوض او في مجرى المياه و تاكد قبل رمي المادة الصلبة انها لا تسبب اشعال النار فيما لو تعرضت للهواء او انها تعطي روائح غير مرغوب فيها عند عند رميها في الحوض او مجاري المياه

- لا تسكب الماء ابدا في حامض الكبريتيك المركز لغرض تخفيف الحامض الطريقة السليمة لتخفيف حامض الكبريتيك المركز هي باضافة الحامض المركز ببطيء و عناية الى الماء في وعاء زجاجي(انبوب اختبار مناسب او اسطوانة مدرجة او كاس زجاجي او قنينة زجاجية الخ) مع التحريك المستمر فاذا اقتربت درجة حرارة المحلول من مرحلة الغليان عند ذلك يجب تبريده بسكب ماء الحنفية على الجدران الخارجية للوعاء و الاستمرار بالتحريك لحين انخفاض درجة الحرارة ثم يباشر باضافة الحامض كالسابق

- احذر عند تسخين مادة صلبة او سائلة في انبوبة اختبار ان تكون فوهة الانبوبة موجهة نحوك او نحو زميل مجاور لك او باتجاهادوات المختبر وكذلك نفس الحال عند غلي محلول او سائل

- لا تحاول ابدا تذوق اي مادة كيميائبة سائلة او صلبة تتعامل معها في المختبر و لا تشرب الماء في اي وعاء زجاجي تستخدمه في عملك داخل المختبر اذكر دائما ان من حولك العديد من المواد السامه

- كن حذرا عندما تريد شم سائل او غاز يتصاعد اثناء تفاعل ما و لا تشم بخار السائل او الغاز المتصاعد من قنينة او انبوبة اختبار او دورق التفاعل بتقريب الفوهة من الانف

- اجراء عملية التسخين داخل الهود(خزانات الغاز) لان عملية التسخين يتضمن تحرير ابخرة او غازات ذات رائحة كريهه او سامة

- ينبغي على الطالب عدم لبس الحلي الذهبيه و الفضية وغيرهما اثناء العمل خشية لتعرضها للتلف

Analytical chemistry

Is the science of the characterization and measurement of chemicals and also involve separating, identifying and determining the relative amounts of the components in a sample of matter. Chemical analysis is divided into two types:

Chemical analysis

Quantitative analysis ***Qualitative analysis***

Qualitative analysis

The term **Qualitative analysis** involves the method by which the constituents of materials are identified. Three different methods of operation used in **Qualitative** analysis depending upon the amount of sample used. Macro on **Qualitative** analysis. For example; is applied when the solution being analyzed has a volume ranging from 5 to 100 ml or more. And in the case of solid samples, an amount of I g or more are often used. The semi micro method involves the use of smaller quantities of materials ranging, in solid, from 1 mg. to 1 g. and in liquid from 1 drop (about 0.05 ml) to 1 ml.

Positively charged ions are termed cations (i.e. cathode ions) because, in an electrolysis cell, they migrate toward the negative electrode. Positively charged inorganic ions or inorganic cations are, sometimes, called metallic ions, and are generally prodused by the ionization of inorganic salts and bases.

In this scheme twenty four cations of of common occurrence are involved. By taken advantage of the differences in chemical properties, those cations are divided into five major group. Four of the groups are precipitated and separated from each other through group reagents, whereas the fifth is a soluble one.

Group I (Ag^+, Pb^{2+}, Hg_2^{2+}) cations: produce insoluble chlorides so they can be precipitated with dilute HCl, while all other cations remain in solution.
Group II (Cu^{2+}, Bi^{3+}, Cd^{2+}, Hg^{2+}, As^{3+}, Sb^{3+}, Sn^{4+}) cations: produce very insoluble sulfides so they can be precipitated by low amounts of sulfide ion; this can be achieved by adding an acidic solution of H_2S.
Group III (Al^{3+}, Cr^{3+}, Fe^{3+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}) cations: produce slightly soluble sulfides so they can be precipitated by relatively high amounts of sulfide ion; this can be achieved by adding a basic solution of H_2S.
Group IV (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) cations, as well as all of the above groups, produce insoluble carbonates so they can be precipitated by the addition of carbonate once the ions of the first three groups have been removed.
Group V (Na^+, K^+, NH_4^+) cations do not precipitate with any of the above reagents.

Group I Analysis

Ag^+, Pb^{2+}, Hg_2^{2+}

The silver group is composed of three cations namely silver ion Ag^+, mercury (I), Hg_2^{++}, and lead (II), Pb^{++}. Chemistry of the Precipitation of the Group I Cations The precipitating reagent of Group I is a dilute solution of hydrochloric acid, and the ions precipitated are those of silver, Ag^+, mercury (I), Hg_2^{++}, and lead (II), Pb^{++}.

A. Identification of the Silver ion Ag^+

A list of some of the insoluble Silver compounds is given in table 1 below:

Table 1 Insoluble silver compounds with their colors

	Compound	color
	$Ag_2C_2O_4$	White
*	Ag_2CrO_4	Red
	Ag_2CO_3	Yellow
	$AgOH$	Brownish black
	$AgCl$	White
	$AgCN$	White
	$AgCNS$	White
	$AgBr$	Pal yellow
↓	AgI	Yellow
	Ag_2S	Grey-black

* Decreasing Concentration of Ag^+ Ion

1. Chloride ion solution (use dilute HCl)
   When a dilute hydrochloric acid is added to silver ions solution. a white precipitate of silver chloride, AgCl is formed.

$$Ag^+ + Cl^- \rightleftharpoons \underset{\text{White ppt.}}{AgCl\downarrow}$$

a) AgCl chemical decomposition when exposed to ultraviolet or to a strong sun light (distinction from $PbCl_2$ and Hg_2Cl_2). This method or identification is very sensitive with U.V. light. Place a drop of the test solution on a filter paper, followed by a drop of dilute HCl. Expose the filter paper containing the precipitation to U.V. light Appearance of a purple-gray or grayish-black spot indicates the silver ion.

b) AgCl is soluble in aqueous ammonia (ammonia water ammonium hydroxide)due to the formation of the silver ammonia complex $Ag(NH_3)_2^+$

$$Ag\,Cl + 2NH_4OH \rightleftharpoons Ag(NH_4)_2^+ + Cl^-$$

$Ag(NH_4)_2^+$ ion is destroyed upon acidifying the solution with nitric acid reprecipitating AgCl.

$$Ag(NH_3)_2^+ + Cl^- + 2\,H_3O^+ \rightleftharpoons \underset{\text{White ppt.}}{AgCl\downarrow} + 2NH_4^+ + 2H_2O$$

2. 8-quinolinol solution (8-hydroxy quinolone or oxime).
   When this reagent is added to a solution containing silver ions. a yellow precipitate of silver 8- quinolinolate, AgC_9H_6NO, is formed, in the present of ammonium acetate.

$$Ag^+ + C_9H_6NOH + H_2O \rightleftharpoons \underset{\text{Yellow ppt.}}{AgC_9H_6NO\downarrow} + H_3O^+$$

3. Iodide ion solution(use KI solution)
   Iodide ion precipitates the silver ion as yellow silver iodide, AgI.

$$Ag^+ + I^- \rightleftharpoons \underset{\text{Yellow ppt.}}{AgI\downarrow}$$

AgI is soluble in both solutions of potassium cyanide.

$$AgI + 2CN^- \rightleftharpoons \underset{\text{Coloreless}}{Ag(CN)_2^-} + I^-$$

And sodium thiosulfate

$$AgI + 2S_2O_3^= \rightleftharpoons Ag(S_2O_3)_2^{3-} + I^-$$

4. Chromate ion solution(use K_2CrO_4solution)
   Silver ion and chromate ion combine to form a red precipitate of silver chromate, Ag_2CrO_4, which is insoluble in dilute acetic acid but soluble in nitric acid and in aqueous ammonia.

$$2Ag^+ + CrO_4^= \rightleftharpoons \underset{\text{Red.}}{Ag_2CrO_4\downarrow}$$

B. Identification of the Lead ion Pb^{2+}

A list of some of the insoluble mercuric compounds is given in table 2 below:

Table 2 Insoluble lead compounds with their colors

	Compound	color
	$PbCl_2$	White
*	$PbBr_2$	White
	PbF_2	White
	PbI_2	Orang-yellow
	$PbSO_4$	White
	$Pb(OH)_2$	White
	PbC_2O_4	White
	$PbCO_3$	White
↓	$PbCrO_4$	Yellow
	$Pb_3(PO_4)_3$	White
	PbS	black

* Decreasing Concentration of Pb^{++} Ion

1. Chloride ion solution (use dilute HCl)
   When a dilute hydrochloric acid is added to lead ions solution. a white precipitate of lead chloride, $PbCl_2$ is formed.

$$Pb^{++} + 2Cl^{-} \rightleftharpoons \underset{\text{White ppt.}}{PbCl_2\downarrow}$$

a) $PbCl_2$ chemical decomposition is **not affected** by ultraviolet or to a strong sun light (distinction from AgCl and Hg_2Cl_2).

b) $PbCl_2$ is soluble in hot water, but separates again, as white upon cooling the solution.

2. Sulfate ion solution (use dilute H_2SO_4).
   Lead ion and sulfate ion combine to form a white precipitate of lead sulfate ($PbSO_4$)

$$Pb^{++} + SO_4^{=} \rightleftharpoons \underset{\text{White ppt.}}{PbSO_4\downarrow}$$

$PbSO_4$ is soluble in concentrated solution of ammonium acetate.

$$PbSO_4 + 2C_2H_3O_2^{-} \rightleftharpoons \underset{\text{In solution}}{Pb(C_2H_3O_2)_2} + SO_4^{2-}$$

3. Chromate ion solution(use K_2CrO_4solution)
   Lead ion and chromate ion combine to form a yellow precipitate of lead chromate, $PbCrO_4$.

$$Pb^{++} + CrO_4^{=} \rightleftharpoons \underset{\text{Yellow ppt.}}{PbCrO_4\downarrow}$$

$PbCrO_4$, which is soluble in nitric acid and in alkali hydroxides.

$$PbCrO_4 + H_3O^{+} \rightleftharpoons Pb^{++} + HCrO_4^{-} + H_2O$$
$$PbCrO_4 + 4OH^{-} \rightleftharpoons PbO_2^{2-} + CrO_4^{2-} + 2H_2O$$

4. Sulfide ion solution (use H_2S which means Thioacetamide CH_3CSNH_2)
   Lead ion and sulfide ion combine to form a black precipitate of lead sulfide, PbS.

$$Pb^{++} + H_2S + 2H_2O \rightleftharpoons \underset{\text{Black ppt.}}{PbS\downarrow} + 2\,H_3O^{+}$$

PbS, which is soluble in hot dilute nitric acid.

$$3PbS + 8\,H_3O^{+} + 2NO_3^{-} \rightleftharpoons 3Pb^{++} + 2NO + 12\,H_2O + 3S^{-}$$

C. Identification of the Mercurous ion Hg_2^{2+}

A list of some of the insoluble mercurous compounds is given in table 3 below:

Table 3 Insoluble mercurous compounds with their colors

Compound	color
Hg_2Cl_2	White
* $Hg_2C_2O_4$	White
Hg_2Br_2	Whitish yellow
Hg_2CO_3	Yellowish brown
Hg_2I_4	Yellow
Hg_2S	black

* Decreasing Concentration of Hg_2^{++} Ion

1. Chloride ion solution (use dilute HCl)
   When a dilute hydrochloric acid is added to mercurous ions solution. a white precipitate of mercurous chloride, Hg_2Cl_2 is formed.

$$Hg_2^{++} + 2Cl^- \rightleftharpoons \underset{\text{White ppt.}}{Hg_2Cl_2\downarrow}$$

a) When Hg_2Cl_2 exposed to ultraviolet or to a strong sun light a bright reddish orange fluorescence is noticed (distinction from $PbCl_2$ and AgCl).

b) Hg_2Cl_2 turns to a black mixture when treated with aqueous ammonia.

$$Hg_2Cl_2 + 2NH_3 \rightleftharpoons \underset{\text{White ppt.}}{HgNH_2Cl\downarrow} + \underset{\text{Black ppt.}}{Hg\downarrow} + NH_4^+ + Cl^-$$

This mixture of $HgNH_2Cl$ and Hg is soluble in concentrated nitric acid.

$$2HgNH_2Cl + 4H_3O^+ + 2NO_3^- \rightleftharpoons 2Hg^{++} + N_2 + 2NO + 8\,H_2O + 2Cl^-$$

$$3Hg + 8H_3O^+ + 2NO_3^- \rightleftharpoons 3Hg^{++} + 2NO + 12\,H_2O$$

2. Aqueouse Ammonia
   Mercurous ions form when react with aqueouse ammonia a black precipitate of finely divided mercury

$$2Hg_2^{++} + 4NH_{3\ aq.} + H_2O \rightleftharpoons Hg_2ONH_2^+ + \underset{\text{Black}}{2Hg\downarrow} + 3NH_4^+$$

3. 8-quinolinol solution (8-hydroxy quinolone or oxime).
   When this reagent is added to a solution containing mercurous ions. Gelatinous yellow precipitate of mercurous 8- quinolinolate, $Hg_2(C_9H_6NO)_2$, is formed, in the present of ammonium acetate.

$$Hg_2^{++} + 2C_9H_6NOH + 2H_2O \rightleftharpoons \underset{\text{Yellow ppt.}}{Hg_2(C_9H_6NO)_2\downarrow} + H_3O^+$$

The precipitate changes its color from yellow to yellowish orange, to orange and then to dark orange in about five minutes.

4. Stannous chloride solution ($SnCl_4$ solution)

Stannous chloride reduces the mercuric ion to the mercurous ion giving a white precipitate of Hg_2Cl_2.

$$2Hg_2^{2+} + 2Cl^- \rightleftharpoons \underset{\text{White ppt.}}{Hg_2Cl_2\downarrow} + SnCl_6^=$$

Excess of the stannous chloride solution causes the reduction of mercurous chloride, first formed, to black metallic mercury).

$$Hg_2Cl_2 + SnCl_4^= \rightleftharpoons \underset{\text{Black ppt.}}{2Hg\downarrow} + SnCl_6^=$$

The principle of separation

Due to the fact that only AgCl, $PbCl_2$ and Hg_2Cl_2 are slightly soluble in dilute acid solutions, the ions Ag^+, Pb^{++} and Hg_2^{++} can be separated from the rest of the cations by the addition of chloride ions.

$$Ag^+ + Cl^- \rightleftharpoons \underset{\text{White ppt.}}{AgCl\downarrow}$$

$$Pb^{++} + 2Cl^- \rightleftharpoons \underset{\text{White ppt.}}{PbCl_2\downarrow}$$

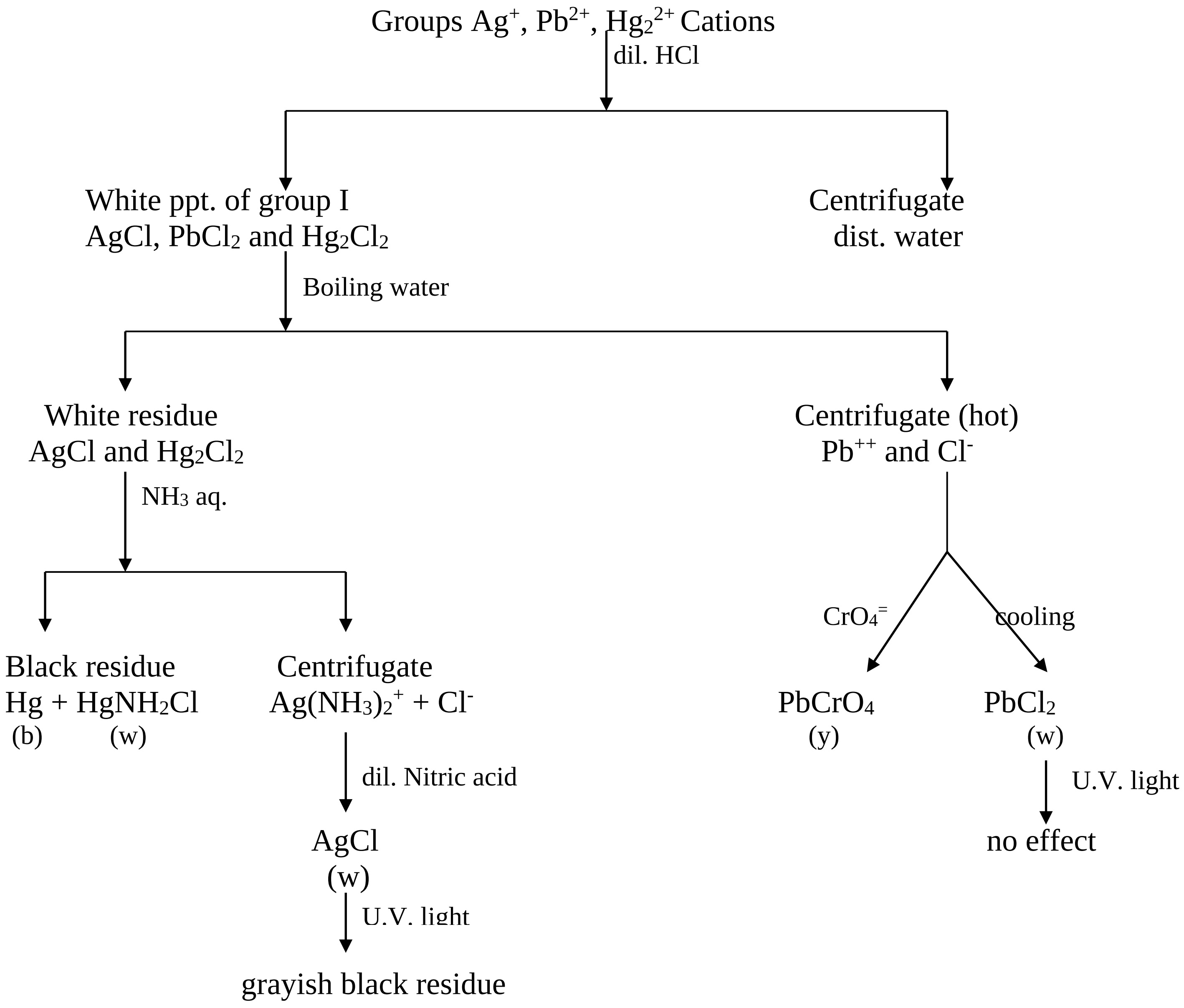
$$Hg_2^{++} + 2Cl^- \rightleftharpoons \underset{\text{White ppt.}}{Hg_2Cl_2\downarrow}$$

Lead chloride can separated from AgCl and Hg_2Cl_2 by treating the chloride mixture with boiling water. Lead ion is then detected, in the filtrate, by the addition of the chromate ion.

Silver chloride is separated from mercurous chloride, on the basis of its solubility in aqueous ammonia which produces the complex ion, $Ag(NH_3)_2^+$. For the identification of silver ion, the solution containing this complex ion is acidified by nitric acid, thus AgCl if formed again.

Aqueous ammonia, not only dissolves AgCl but, also, converts Hg_2Cl_2 to a grayish black residue which is a mixture of $HgNH_2Cl$ and Hg. This black residue serves as a good indication for the presence of Hg_2^{++}.

Analysis of group I cations



The unknown solution

A 10 ml unknown solution will be provided to each student, only after the completion of the analysis of the known solution. The student should use 5 ml and save the rest to be used in case of loss of the first portion accidentally during the analysis or, when repetition of the work becomes necessary.

Procedure NO. I Separation and identification of Group I cations

<table>
<tr><td colspan="3">Precipitation of the group
Place 10 drops of the given solution in a test tube and add 3 drops of 3M HCl (1). Heat the mixture in a water bath a few minutes, cool under the tap and allow the ppt. to settle. test for complete ppt. centrifuge and save the centrifuge , wash the ppt. with 10 drops of cold water containing a few drops of 3M HCl (2).</td></tr>
<tr><td colspan="2">Precipitate:
White ppt. which may be AgCl, Hg_2Cl_2 and $PbCl_2$ wash twice with 7 drops portion of boiling water and combine washings (3).</td><td>Centrifugate
Dist. water</td></tr>
<tr><td rowspan="2">Centrifugate:
May contain Pb^{++} and Cl^- ions. Divide, while still hot, into two parts:
Small part:
Add a few drops of 1M K_2CrO_4 solution, yellow ppt. of $PbCrO_4$ confirms presence of Pb^{++}ion.
Large pare:
Evaporate to half its volume cool to room temperature. formation of white crystalline ppt. not affected by U.V. light confirms Pb^{++}.</td><td colspan="2">Residue :
May contain AgCl and Hg_2Cl_2. Apply the U.V. light test on a small part of the ppt. (4). Blackening confirms Ag^+ ion, but reddish orange fluorescence confirms Hg_2^{++}ion. If the silver ion is present the identification of Hg_2^{++}ion. May not be clear. In this case, treat the white ppt. with 10 drops of 3M warm aqueous ammonia, then centrifuge.</td></tr>
<tr><td>Centrifugate
May contain $Ag(NH_3)_2^+$ and Cl^- ions which give in nitric acid a white ppt. of AgCl indicating the presence of Ag^+ ion.</td><td>Residue:
If black, due to $(Hg+HgNH_2Cl)$.Hg_2^{++} ion is confirmed.</td></tr>
</table>

Notes on procedure No. I

1. slight excess of dilute hydrochloric acid decreases the solubility of the chloride thus, cases more complete precipitation. But large excess of a HCl or large concentration of the chloride ion should be avoided since it will partially dissolve AgCl and $PbCl_2$ through the formation of complex ion.
   $AgCl + Cl^- \longrightarrow AgCl_2^-$
   $AgCl + 2Cl^- \longrightarrow AgCl_2^=$
   $PbCl_2 + 2Cl^- \longrightarrow PbCl_4^=$

2. if the wash water contains no HCl, an appreciable amount of $PbCl_2$ will dissolving during the process of washing. The presence of hydrochloric decreases the solubility of lead chloride due to the common ion effect.
3. since $PbCl_2$ is fairly soluble in hot water , its solution should be kept hot when the test for Pb^{++} with $CrO_4^=$ is performed. Otherwise lead ion may not be confirmed.
4. the ultra violet test for the silver ion is very sensitive and reliable. Silver chloride is always easy to identify. But unless Hg_2Cl_2 is present in a relatively large quantity, it can not be detected since the grayish black color of the decomposed AgCl masks the reddish orange color of the fluorescent mercurous chloride.

Report sheet

Analysis of group I cations

Name:……………………………… Unknown No.:……………………..

Section:……………………………. Date:……………………………….

Notes and Equations :

Ions of group I	*Ions found, by the student*	*Ions present in the unknown solution*	*grade*
Ag^+ Pb^{++} Hg_2^{++}			

Signature of the student

Signature of the grader

Group II Cations

Pb^{++}, Hg^{++}, Bi^{+++}, Cu^{++}, Cd^{++}

The cations of this group are characterized by being precipitated the sulfides from a solution which is 0.3M with respect to hydrochloric acid. The precipitating reagent for this group is either hydrogen sulfide, H_2S, or thioacetamide, CH_3CSNH_2. The latter is a source of H_2S. It is very soluble in water and hydrolyzes rapidly in aqueous solution with the liberation of hydrogen sulfide specially at a temperature higher than room temperature.

$$CH_3CSNH_2 + H_2O \rightleftharpoons CH_3CONH_2 + H_2S\uparrow$$

H_2S can also be generated by gentle heating of a mixture called, Aitch-Tu-Ess which is composed of sulfur, paraffin and asbestos.

A. Identification of the Mercuric ion Hg^{++}

A list of some of the insoluble mercuric compounds is given in table 4 below:

Table 4 Insoluble mercuric compounds with their colors

Compound	color
$Hg(IO_3)_2$	White
* $HgBr_2$	White
$Hg(CNS)_2$	White
HgI_2	Red or yellow
↓ HgS	black

* Decreasing Concentration of Hg^{++} Ion

1. Sulfide ion solution (use H_2S or 1M CH_3CSNH_2 sol)

Mercuric ion and sulfide ion combine to form a black precipitate of mercuric sulfide, HgS.

$$Hg^{++} + H_2S^{*} + 2H_2O \rightleftharpoons \underset{\text{Black ppt.}}{HgS\downarrow} + 2H_3O^{+}$$

HgS is soluble in sodium sulfide solution and also in aqua regia (3 volumes of concentrated hydrochloric acid and 1 volume of concentrated nitric acid).

$$3HgS + 2NO_3^{-} + 8H_3O^{+} + 12Cl^{-} \rightleftharpoons 3\,HgCl_4^{=} + 2NO + 3S + 12H_2O$$

---

* H_2S is written here in its molecular form instead of $S^{=}$ ion, since it is slightly ionized (i.e. weak electrolyte).

2. Stannous chloride solution

Stannous chloride reduces the mercuric ion to the mercurous ion giving a white precipitate of Hg_2Cl_2.

$$SnCl_4^{=} + 2HgCl_2 \rightleftharpoons SnCl_6^{=} + \underset{\text{White ppt.}}{Hg_2Cl_2\downarrow}$$

(Mercuric chloride was used as the source of Hg^{++} ions, and was written in its molecularformula because it is a weak salt).

Excess of the stannous chloride solution causes the reduction of mercurous chloride, first formed, to black metallic mercury).

$$SnCl_4^{=} + Hg_2Cl_2 \rightleftharpoons \underset{\text{Black ppt.}}{2Hg\downarrow} + SnCl_6^{=}$$

3. Iodide Ion solution (use KI solution).

The dropwise addition potassium iodide solution to a solution containing mercuric ions produces a red precipitate of mercuric iodide, HgI_2

$$Hg^{++} + 2I^{-} \rightleftharpoons \underset{\text{Red ppt.}}{HgI_2\downarrow}$$

HgI_2 is soluble in excess of KI solution to the formation of the mercuric-iodide complex ion, $HgI_4^{=}$.

$$HgI_2 + 2I^{-} \rightleftharpoons HgI_4^{=}$$

4. Cobaltous- Thiocyanate reagent

With the mercuric ion, this reagent gives a deep blue precipitate of cobaltous mercuric thiocyanate, $HgCo(CNS)_4$. The reaction is carried out by adding, to 1 ml of the solution containing Hg^{++} ions, about 1 ml of 3M sodium acetate solution and about 0.5 ml of 0.1M $Co(NO_3)_2$ solution and stirring thoroughly with dropwise addition of 0.1M ammonium thiocyanate solution.

$$Hg^{++} + Co^{++} + 4CNS^{-} \rightleftharpoons \underset{\text{Deep blue ppt.}}{HgCo(CNS)_4\downarrow}$$

B. Identification of the Bismuth ion Bi^{+++}

A list of some of the insoluble bismuth compounds is given in table 5 below:

Table 5 Insoluble bismuth compounds with their colors

Compound		color
	BiOCl	White
*	BiI_3	Reddish or brownish-gray
	$BiAsO_4$	White
	(BiO)OH	White
	$BiPO_4$	White
	$Bi(OH)_3$	White
↓	Bi_2S_3	Brown

* Decreasing Concentration of Bi^{+++} Ion

1. Sulfide ion solution (use H_2S or CH_3CSNH_2)

Bismuth ion and sulfide ions give a brown-black precipitate of bismuth sulfide, Bi_2S_3.

$$2Bi^{+++} + 3H_2S + 6H_2O \rightleftharpoons \underset{\text{Brown-black ppt.}}{\overset{\downarrow}{Bi_2S_3}} + 6H_3O^+$$

Bi_2S_3 is insoluble in cold dilute acids, but soluble in boiling hydrochloric acid and in hot dilute nitric acid.

$$Bi_2S_3 + 2NO_3^- + 8H_3O^+ \rightleftharpoons 2Bi^{+++} + 2NO + 3S + 12H_2O$$

2. Aqueous ammonia

Bismuth forms a white precipitate of bismuth hydroxide, $Bi(OH)_3$, when reacts with aqueous ammonia.

$$Bi^{+++} + 3NH_3\,\text{aq.} + 3\,H_2O \rightleftharpoons \underset{\text{White ppt.}}{Bi(OH)_3\downarrow} + 3NH_4^+$$

$Bi(OH)_3$ is insoluble in excess of the precipitating reagent.

3. Stannite ion, $SnO_2^=$, (each student prepares his solution).

Bismuth ions give a black precipitate of finely divided metallic bismuth when react with stannite ions. To prepare sodium stannite, Na_2SnO_2, solution add 3M NaOH solution drop by drop to a stannous chloride solution until the white precipitate of stannous hydroxide, $Sn(OH)_2$, just disappears.

$$Sn^{++} + 2OH^- \rightleftharpoons \underset{\text{White ppt.}}{Sn(OH)_2\downarrow}$$

$$Sn(OH)_2 + 2OH^- \rightleftharpoons SnO_2^= + 2H_2O$$

$$2Bi^{+++} + 3SnO_2^= + 6OH^- \rightleftharpoons 2Bi + 3SnO_3^= + 3H_2O$$

or $$2Bi(OH)_3 + 3SnO_2^= \rightleftharpoons \underset{\text{Black ppt.}}{2Bi\downarrow} + 3SnO_3^= + 3H_2O$$

C. Identification of the Cupric ion Cu^{++}

A list of some of the insoluble bismuth compounds is given in table 6 below:

Table 6 Insoluble bismuth compounds with their colors

Compound	color
$Cu(IO_3)_2$	Blue
* $CuCrO_4$	brown
CuC_2O_4	Bluish-white
$CuCO_3$	Blue
$Cu_2Fe(CN)_6$	Red-brown
$Cu(OH)_2$	Blue
CuS	Black

* Decreasing Concentration of Cu^{++} Ion

1. Sulfide ion solution (use H_2S or CH_3CSNH_2)

Cupric ion and sulfide combine to form a black precipitate of cupric sulfide, CuS.

$$Cu^{++} + 3H_2S + 2H_2O \rightleftharpoons \underset{\text{Black ppt.}}{CuS\downarrow} + 2H_3O^+$$

CuS is insoluble in sodium or potassium hydroxide, but soluble in hot dilute nitric acid.

$$3CuS + 2NO_3^- + 8H_3O^+ \rightleftharpoons 3Cu^{++} + 2NO + 3S + 12H_2O$$

2. Aqueous ammonia

Cupric ion forms with aqueous ammonia the deep blue color solution of tetra ammine cupric complex ion, $Cu(NH_3)_4^{++}$.

$$Cu^{++} + 4NH_3 \text{ aq.} \rightleftharpoons \underset{\text{Deep blue}}{Cu(NH_3)_4^{++}}$$

The deep blue color of the complex ion fades out upon acidifying the solution, due to the destruction of the complex ion.

$$Cu(NH_3)_4^{++} + 4H_3O^+ \rightleftharpoons Cu^{++} + 4NH_4^+ + 4H_2O$$

3. 8-quinolinol solution (known as 8-hydroxy quinoline or oxine).

A light green precipitate of cupric 8-quinolinolate, $Cu(C_9H_6NO)_2$, is formed when cupric ion reacts with this reagent in a solution saturated ammonium acetate.

$$Cu^{++} + 2C_9H_6NOH + 2H_2O \rightleftharpoons \underset{\text{Green ppt.}}{Cu(C_9H_6NO)_2\downarrow} + 2H_3O^+$$

The precipitate has a low solubility in acetone and in ethanol.

4. Potassium ferrocyanide solution (use $K_4[Fe(CN)_6]$ solution).

A reddish-brown precipitate is formed when cupric ions react with potassium ferrocyanide solution.

$$2Cu^{++} + K_4[Fe(CN)_6] \rightleftharpoons \underset{\text{Reddish-brown ppt.}}{Cu_2[Fe(CN)_6]\downarrow} + 4K^+$$

5. Iodide ion solution (use KI or NaI solution)

A yellowish- brown mixture of Cu_2I_2 (white) and I_2 (yellowish brown) precipitate is formed when cupric ions react with Iodide.

$$2Cu^{++} + 4I^- \rightleftharpoons Cu_2I_2\downarrow + I_2 \text{ (yellowish- brown ppt.)}$$

$$I_2 + I^- \rightleftharpoons I_3^-$$

D. Identification of the Cadmium ion Cd^{++}

A list of some of the insoluble bismuth compounds is given in table 7 below:

Table 7 Insoluble cadmium compounds with their colors

Compound	color
$Cd(CN)_2$	White
* CdC_2O_4	White
$Cd(OH)_2$	White
$Cd_3(AsO_4)_2$	White
$CdCO_3$	White
↓ CdS	Yellow-orange

* Decreasing Concentration of Cd^{++} Ion

1. Sulfide ion solution (use H_2S or CH_3CSNH_2)

Cadmium ion and sulfide combine in a neutral or a slightly acidic solution to form a yellow precipitate of cadmium sulfide, CdS. Which soluble in hot dilute nitric acid and also in hot diluted sulfuric acid but insoluble in KCN solution.

$$Cd^{++} + H_2S + 2H_2O \rightleftharpoons \underset{\text{Yellow ppt.}}{CdS\downarrow} + 2H_3O^+$$

2. Aqueous ammonia

A white precipitate of cadmium hydroxide, $Cd(OH)_2$, is formed when cadmium ion reacts with aqueous ammonia.

$$Cd^{++} + 2NH_3\text{ aq.} + 2H_2O \rightleftharpoons \underset{\text{White ppt.}}{Cd(OH)_2\downarrow} + 2NH_4^+$$

$Cd(OH)_2$ is soluble in excess of the precipitant due to the formation of cadmium tetrammine complex ion $Cd(NH_3)_4^{++}$.

$$Cd(OH)_2 + 4NH_3\text{ aq.} \rightleftharpoons Cd(NH_3)_4^{++} + 2OH^-$$

3. 8-quinolinol solution (known as 8-hydroxy quinoline or oxine).

A light greenish yellow precipitate of cadmium 8-quinolinolate, $Cd(C_9H_6NO)_2.2H_2O$, is formed when cadmium ion reacts with this reagent in a solution saturated ammonium acetate.

$$Cd^{++} + 2C_9H_6NOH + 2H_2O \rightleftharpoons \underset{\text{Greenish-yellow ppt.}}{Cd(C_9H_6NO)_2\downarrow} + 2H_3O^+$$

The precipitate fluoresces intensely pale green in ultra-violet light, and is insoluble in acetone or ethanol.

The principle of separation of group II cations

The copper group of the cations is composed of five cations which are precipitated as sulfides from a solution 0.2-0.3M in H_3O^+ ions using hydrochloric acid, and hydrogen sulfide or thioacetamide as the precipitating agent. Under this condition group II cations are separated from those of the subsequent groups.

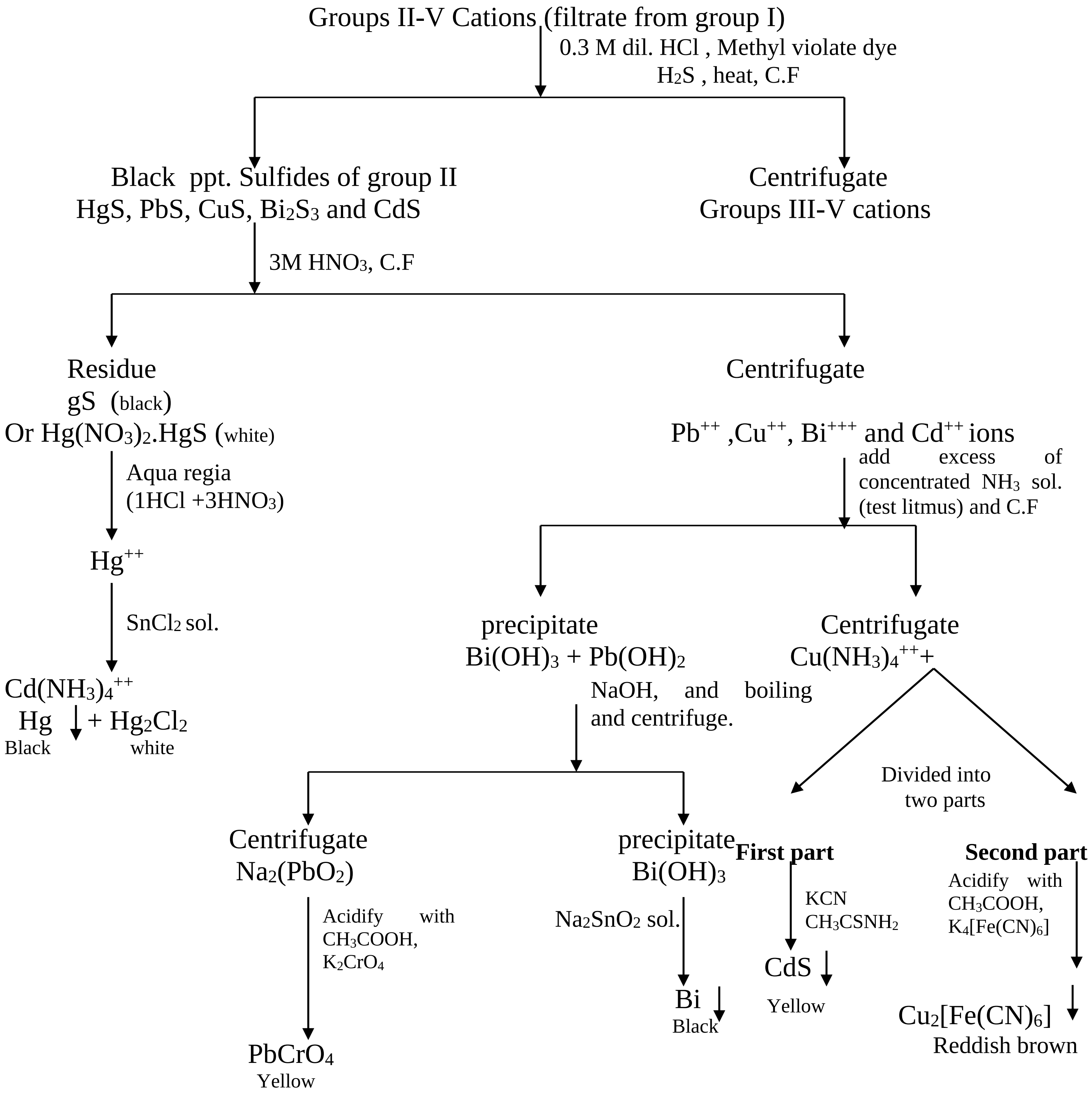
Not only the sulfides of group II cations are insoluble in water but also some of the sulfides group III cations. It can be seen from the table below that all the sulfides involved can be considered as beining very slightly soluble, and vary widely in their solubilities.

Insoluble sulfides of some cations from group II and group III with their solubility product constants table (8)

Sulfide from group II (insoluble in 0.3M HCl)		Sulfide from group III (soluble in 0.3M HCl)	
Sulfide	Ks.p.	Sulfide	Ks.p.
PbS	3.4×10^{-28}	MnS	1.4×10^{-15}
CdS	3.6×10^{-29}	FeS	3.7×10^{-19}
CuS	8.5×10^{-45}	CoS	7.0×10^{-23}
HgS	3.0×10^{-53}	ZnS	3.0×10^{-23}
Bi_2S_3	1.6×10^{-72}	NiS	1.4×10^{-24}
Sb_2S_3	1.6×10^{-93}		

The copper group

Analysis of group II cations



Procedure NO. 2 Separation and identification of Group II cations

<table>
<tr><td colspan="5">Precipitation of the group
Place 10 drops of the given solution in a test tube and adjust the acidity to 0.3M HCl (1) by using 1M HCl. Add 10 drops of H_2S and then heat to boiling for a few minutes, centrifuge and test the solution for complete precipitation of the group cations as sulfides by heating and passing H_2S again stirr well and centrifuge.</td></tr>
<tr><td colspan="4">Precipitate:
Add 10 drops of 3M HNO_3 upon the ppt. with stir, and heat in water bath for 3 minutes and centrifuge .</td><td>Centrifugate
Groups III-V cations</td></tr>
<tr><td colspan="2">Precipitate:
May contain HgS (b) or $Hg(NO_3)_2.2HgS$ (w), dissolve in 5 drops of aqua regia, add 10 drops of water, then heat for about 3 minutes (under hood). Cool then add 2 drops of $SnCl_2$ sol. white ppt. , Hg_2Cl_2 or gray ($Hg + Hg_2Cl_2$) confirms presence of Hg^{++} ion.</td><td colspan="3">Centrifugate
Contains Pb^{++}, Bi^{+++}, Cu^{++} and Cd^{++} ions. Make the sol. basic by dropwise addition of concentrated aq. Ammonia with stirring until about 3 drops in excess of conc. NH_3 has been added (test litmus). Then centrifuge.</td></tr>
<tr><td colspan="3" rowspan="2">Precipitate :
This ppt. contains the hydroxides of Pb^{++} and Bi^{+++} as $Pb(OH)_2$, $Bi(OH)_3$, add 4 drops of NaOH and place in the boiling water for 2 min. and centrifuge.</td><td colspan="2">Centrfugate :
May be contains $Cu(NH_3)_4^{++}$ and $Cd(NH_3)_4^{++}$ complex ions, if solution is deep blue Cu^{++} ion is confirmed (4). (If necessary concentrate the solution to 1 ml by gentle heating), divide the solution into two parts:</td></tr>
<tr><td colspan="2">First portion :
Add drop by drop carefully of KCN solution until the blue color of the solution disappears (5), add 10 drops of H_2S and boil for 5 min. formation of yellow ppt. of CdS means Cd^{++} ions found.</td></tr>
<tr><td>Centrfriugate:
This solution contains $Na_2[PbO_2]$ which acidify with diluted acetic acid and then add 2 drops of potassium chromate K_2CrO_4 a yellow ppt. of $PbCrO_4$ will appears.</td><td colspan="2">Precipitate :
This white ppt. contains bismuth hydroxide $Bi(OH)_3$, wash with 10 drops of water and prepare sodium stannite (2), (3) to sol. from which 10 drops of are poured upon the ppt. immediate blackening of the ppt. (Bi) confirms Bi^{+++} ion.</td><td colspan="2">Second portion:
Acidify with diluted acetic acid and add 1 drop of potassium ferrocyanide solution, $K_4[Fe(CN)_6]$. The formation of reddish-brown precipitate means the Cu^{++} ions is found.</td></tr>
</table>

Notes on procedure No. II

1- To adjust the acidity to about 0.3M HCl, add 1 drop of Methyl Violate dye to the mixture solution, the Methyl Violate shows different colors at different hydronium ion concentration (different acidity) as shown below:

Color	**Solution**
Violet	neutral and basic
Blue	0.1 M H_3O^+
Blue-green	0.3 M H_3O^+
Yellow-green	0.5 M H_3O^+
Yellow	1.0 M H_3O^+ and higher

$$\text{Blue} \xrightarrow[\text{HCl}]{\text{1 drop}} \text{Green (0.3M)} \xleftarrow[NH_4OH]{\text{1 drop}} \text{Yellow}$$

If the color of solution is blue,
The solution will be alkaline

If the color of solution is yellow,
The solution will be acidic

2- to prepare sodium stannite solution (see the preparation on the Identification of the Bismuth ion Bi^{+++} no. 3) this reagent must be fresh, when used, and made up just before using it, since it undergoes an atmospheric oxidation to sodium stannate, Na_2SnO_3, which is not oxidized by $Bi(OH)_3$.

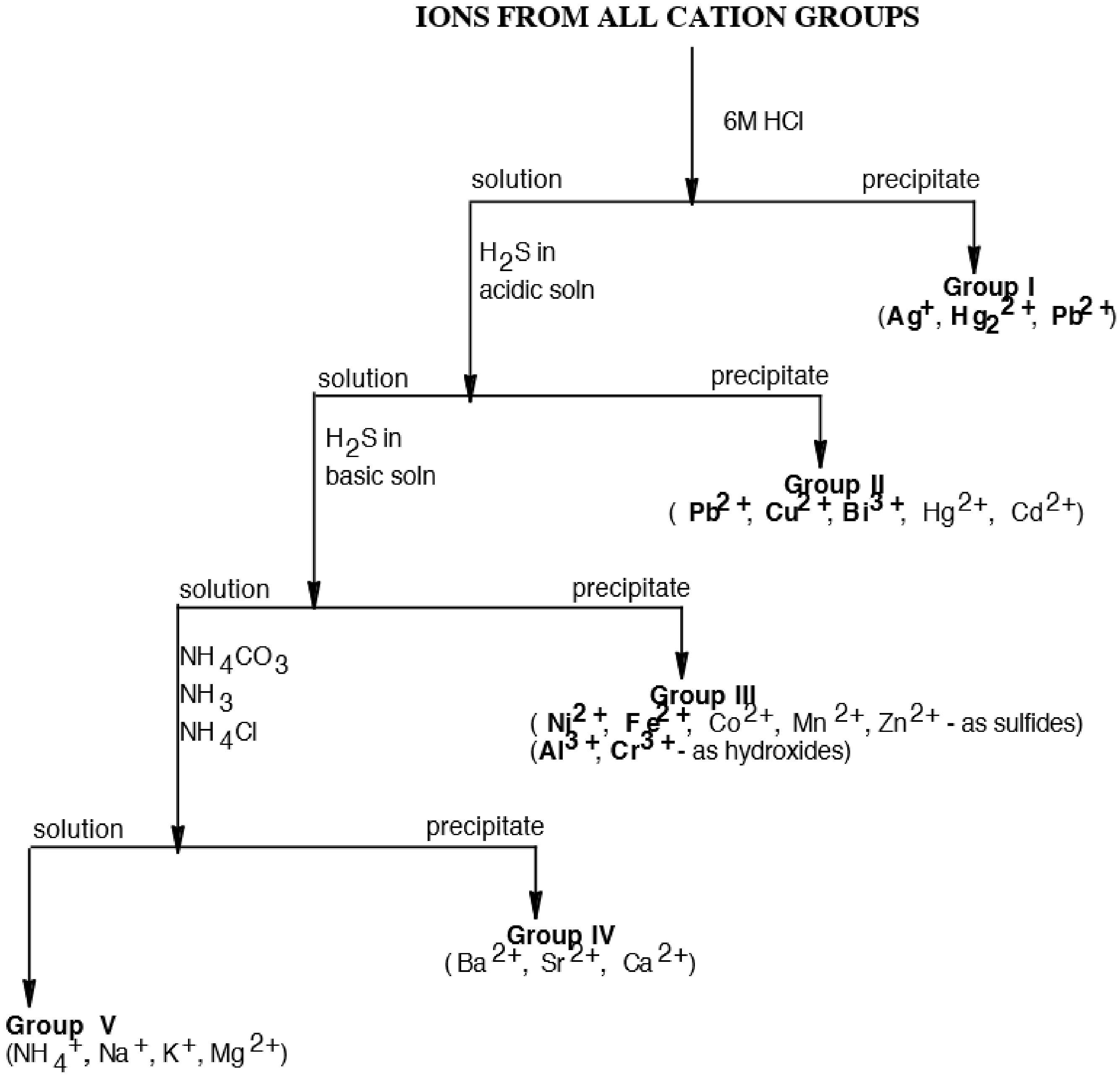
3- the stannite ion, $SnO_2^{=}$, reduces bismuth hydroxide to metallic bismuth, Bi, which is black. Thus bismuth ion is not confirmed unless the precipitate is black and not brown.

4- If the blue color is not quite satisfactory, place 1 ml of the solution in a test tube then acidify with 3M HCl and add a solution of $K_4[Fe(CN)_6]$. the formation of reddish-brown precipitate of $Cu_2[Fe(CN)_6]$ means the Cu^{++} ion is found.

5- potassium cyanide , KCN, solution converts the cupric-ammonia complex ion, $Cu(NH_3)_4^{++}$, to the stable and colorless complex ion, $Cu(CN)_3^{=}$, the later dose not react with hydrogen sulfide, thus no black precipitate of CuS is formed.

Systematic group separation of the cations

The overall scheme for the systematic analysis of a mixtures of cations, based on the five major groups discussed above, is shown as a flow chart below.



Report sheet

Analysis of group II cations

Name:……………………………… Unknown No.:……………………..

Section:……………………………. Date:……………………………….

Notes and Equations :

Ions of group II	***Ions found, by the student***	***Ions present in the unknown solution***	***grade***
Pb^{++} Hg^{++} Bi^{+++} Cu^{++} Cd^{++}			

Signature of the student Signature of the grader

Group III
The Aluminum-Zinc Group
Al^{+++}, Cr^{+++}, Fe^{+++}
Fe^{++}, Co^{++}, Ni^{++}, Mn^{++} and Zn^{++}

This group is composed of eight cations whose chlorides and sulfides are soluble in acidic solution. These cations, above are separated from group IV and V as a mixture of insoluble sulfides and hydroxides in a solution containing ammonia and ammonium chloride , using NH_3 and H_2S or $(NH_4)_2S$ as the precipitating agents.

The insoluble sulfides of group III cations have relatively high solubility product constants, compared with those of group II, (see the table 8) that prevent their precipitation with group II, and the hydroxides have smaller solubility product constants than their corresponding sulfides. Therefore, two precipitating regents are used for the precipitation and separation of cations of this group from those groups IV and V. ammonium sulfide or Fe^{++}, Co^{++}, Ni^{++}, Mn^{++} and Zn^{++} ions, while aqueous ammonia precipitates, as hydroxides the cations Al^{+++}, Cr^{+++}, Fe^{+++}

A . Identification of the aluminum ion, Al^{+++}

A list of some of the insoluble aluminum compounds is given in table 9

Table 9 Insoluble aluminum compounds with their colors

Compound	color
Al_2S_3	White
* $Al(OH)_3$	White
$AlAsO_4$	White
↓ $AlPO_4$	White

* Decreasing Concentration of Al^{+++} Ion

1. Hydroxide ion solution
 a. Aqueous ammonia

A white precipitate of aluminum hydroxide, $Al(OH)_3$, is formed when aluminum ions react with aqueous ammonia. The precipitate is rather $Al_2O_3.xH_2O$

$$2\ Al^{+++} + 6\ OH^- + x\text{-}3\ H_2O \rightleftharpoons \underset{\text{White ppt.}}{Al_2O_3.xH_2O}\downarrow$$

or, $Al^{+++} + 3NH_3\ \text{aq.} + \rightleftharpoons 3H_2O \quad Al(OH)_3 + 3NH_4^+$

The precipitate is insoluble in excess of the precipitating reagent, but soluble in acidic media.

b. Alkali hydroxide solutions.

Aluminum hydroxide is also formed as above but excess of the alkali hydroxide solutions dissolves the precipitate.

$$Al^{+++} + 3OH^- \rightleftharpoons Al(OH)_3$$

$$Al(OH)_3 + OH^- \rightleftharpoons Al(OH)_4^-$$

or, $$Al(OH)_3 + OH^- \rightleftharpoons AlO_2^- + 2H_2O$$

2. 8-quinolinol solution (known as 8-hydroxy quinoline or oxine).

a yellowish green precipitate of 8-quinolinolate, $Al(C_9H_6NO)_3$, is formed in a solution saturated ammonium acetate .

$$Al^{+++} + 3C_9H_6NOH + 3H_2O \rightleftharpoons \underset{\text{Yellow-green ppt.}}{Al(C_9H_6NO)_3\downarrow} + 3\,H_3O^+$$

3. Aluminon solution

The addition of aluminon solution to a basic solution with ammonia containing aluminum ions and ammonium acetate, causes the adsorption of this red organic dye (aluminon) by aluminum hydroxide. No precipitate is actually formed, but a jelly type red precipitate (lake) is produced.

B. Identification of the chromium ion, Cr^{+++}

A list of some of the insoluble chromium compounds is given in table 10

Table 10 Insoluble chromium compounds with their colors

Compound	**color**
* ↓ $Cr(OH)_2$	Yellowish-brown
$Cr(OH)_3$	Yellowish-green
$CrAsO_4$	Light green
$CrPO_4$	Green With ($4H_2O$) or violate (3 OR $6H_2O$)

* Decreasing Concentration of Cr^{+++} Ion

1. Hydroxide ion solution

a. Aqueous ammonia

A gelatinous grayish-green precipitate of chromic hydroxide, $Cr(OH)_3$, is formed when chromic ion react with aqueous ammonia. The precipitate is rather $Cr_2O_3.xH_2O$

$$Cr^{+++} + 3\,NH_3\text{ aq.} + 3H_2O \rightleftharpoons \underset{\text{Grayish-green ppt.}}{Cr(OH)_3} + 3NH_4^+$$

$Cr(OH)_3$ is readily dissolves in acids, but slightly soluble in excess aqueous NH_3 in the cold giving a violate or pink solution of the chromic complex ion, $Cr(NH_3)_6^{+++}$

$$Cr(OH)_3 + 6\,NH_3\text{ aq.} \rightleftharpoons Cr(NH_3)_6^{3+} + 3OH^-$$

b. Alkali hydroxide solutions.

A precipitate similar to the above is formed which is readily soluble in acids and in excess of the alkali hydroxide solutions.

$$Cr^{+++} + 3\ OH^{-} \rightleftharpoons Cr(OH)_3$$

$$Cr(OH)_3 + OH^{-} \rightleftharpoons Cr(OH)_4^{-}$$

or, $$Cr(OH)_3 + OH^{-} \rightleftharpoons \underset{\text{Green}}{CrO_2^{-}} + 2H_2O$$

2. Sodium peroxide Na_2O_2,(or using H_2O_2 and NaOH sol.)

Chromium ion, in the presence of sodium peroxide, is oxidized to the yellow chromate ion $CrO_4^{=}$.

$$Cr^{+++} + 3\ OH^{-} \rightleftharpoons Cr(OH)_3$$

$$Cr(OH)_3 + OH^{-} \rightleftharpoons Cr(OH)_4^{-}$$

$$2Cr(OH)_4^{-} + 3\ O_2^{=} \rightleftharpoons CrO_4^{2-} + 4OH^{-} + 2H_2O$$

The chromate ion is precipitated as a yellow $PbCrO_4$ or $BiCrO_4$

$$CrO_4^{=} + Ba^{++} \rightleftharpoons \underset{\text{Yellow}}{BaCrO_4}$$

$$CrO_4^{=} + Pb^{++} \rightleftharpoons \underset{\text{Yellow}}{PbCrO_4}$$

The addition of H_2O_2 to an acid solution of the chromate ion results in the productions of a blue coloration owing to the formation of CrO_5.

$$HCrO_4^{-} + 2\ H_2O_2 + H_3O^{+} \rightleftharpoons CrO_5 + 4H_2O$$

CrO_5 is unstable in aqueous solution, and readily with the liberation of oxygen.

$$4\ CrO_5 + 12\ H_3O^{+} \rightleftharpoons 4\ Cr^{+++} + 7O_2 + 18H_2O$$

The test for chromium ion may be done as follows:

Precipitate the $CrO_4^{=}$ ion as $PbCrO_4$. dissolve the precipitate in hot 3M HNO_3, cool to room temperature and add equal volume of amyl alcohol followed by about 1 ml 3% H_2O_2. Shake twice and notice the blue color in the alcohol layer which will fade gradually.

C. Identification of the Ferric ion , Fe^{+++}

A list of some of the insoluble ferric compounds is given in table 11 below:

Table 11 Insoluble ferric compounds with their colors

Compound		color
	$Fe_2(SeO_3)_3$	
*	$Fe_4[Fe(CN)_6]_3$	Deep blue
	$Fe(OH)_3$	Reddish brown
	$FePO_4$	Yellowish white
↓	Fe_2S_3	black

* Decreasing Concentration of Fe^{+++} Ion

1. Hydroxide ion solution (NH_3 aq. or alkali hydroxide sol.)

   Ferric ion combines with the hydroxide ions from a reddish-brown precipitate of ferric hydroxide, $Fe(OH)_3$, which is insoluble in excess of the precipitant, but readily dissolves in acids.

$$Fe^{+++} + 3\,NH_3\,aq. + 3H_2O \rightleftharpoons \underset{\text{(Reddish-brown) ppt.}}{Fe(OH)_3} + 3NH_4^+$$

The reddish-brown precipitate does not, actually, correspond to the formula, $Fe(OH)_3$ but rather to the formula $Fe_2O_3.xH_2O$ as it is the case with $Al_2O_3.xH_2O$ and $Cr_2O_3.\ xH_2O$.

$$2\,Fe^{+++} + 6\,OH^- + (x\text{-}3)\,H_2O \rightleftharpoons Fe_2O_3.xH_2O$$

2. Sulfide ion solution (H_2S or $(NH_4)_2S$)

In the presence of hydrochloric acid, hydrogen sulfide reduces ferric ions to ferrous ions with the formation of free sulfur.

$$2\,Fe^{+++} + H_2S + 2H_2O \rightleftharpoons 2Fe^{++} + \underset{\text{Yellow}}{S\downarrow} + 2H_3O^+$$

In a basic solution, hydrogen sulfide or ammonium sulfide solution gives a black precipitate of ferric sulfide, Fe_2S_3

$$2\,Fe^{+++} + 3\,S^= \rightleftharpoons \underset{\text{Black ppt.}}{Fe_2S_3}$$

The precipitate is soluble in dilute hydrochloric acid, which results in the reduction of iron from the ferric state to the ferrous state.

$$Fe_2S_3 + 4\,H_3O^+ \qquad\qquad 2Fe^{++} + 2\,H_2S + 4H_2O + S$$

3. Thiocyanate ion ,CNS^-, solution (use NH_4CNS or KCNS sol.)

   Ferric ion reacts with excess thiocyanate ions to give a deep reddish brown complex ion, $Fe(CNS)_6^{3-}$ or Fe CNS^{++}.

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

$$Fe^{+++} + CNS^- \rightleftharpoons Fe\,CNS^{++}$$

4. 8-quinolinol solution.

   Fine dark green precipitate of ferric 8-quinolinolate, $Fe(C_9H_6NO)_3$, is formed upon adding this regent to a solution containing ferric ions and saturated with ammonium acetate.

$$Fe^{+++} + 3\,C_9H_6NOH + 3H_2O \rightleftharpoons \underset{\text{Dark green ppt.}}{Fe(C_9H_6NO)_3\downarrow} + 3H_3O^+$$

   Ferric ion the only cation in the precipitate entire five groups of the cations that gives such color or the 8-quinolinolate.

D. Identification of the Ferrous ion, Fe^{++}

A list of some of the insoluble ferrous compounds is given in table 12 below:

Table 12 Insoluble ferrous compounds with their colors

Compound		color
	FeC_2O_4	Yellow
*	$Fe(OH)_2$	Pale green or white
	$FeCO_3$	Gray
↓	FeS	Brown-black

* Decreasing Concentration of Fe^{++} Ion

1. Hydroxide ion solution

a. Aqueous ammonia

In the complete absence of air. Ferrous ion and hydroxide ions combine to form a white precipitate of ferrous hydroxide, $Fe(OH)_2$

$$Fe^{++} + 2\,NH_3 + 2\,H_2O \rightleftharpoons \underset{\text{White}}{Fe(OH)_2\downarrow} + 2NH_4^{+}$$

However, the precipitate may look reddish-brown or muddy green, instead of white, due to the quick oxidation of $Fe(OH)_2$ to $Fe(OH)_3$ by the air oxygen.

$$4\,Fe(OH)_2 + 2\,H_2O + O_2 \rightleftharpoons \underset{\text{(Reddish-brown)}}{4\,Fe(OH)_3\downarrow}$$

The precipitate of $Fe(OH)_2$, is insoluble in excess of the precipitate, but soluble in acids.

b. Alkali hydroxide solutions.

Similar results are obtained as in above.

$$Fe^{++} + 2OH^{-} \rightleftharpoons \underset{\text{White}}{Fe(OH)_2\downarrow}$$

2. Sulfide ion solution (H_2S or $(NH_4)_2S$)

No precipitate is formed in acidic solutions when ferrous and sulfide ions are brought together. But a black precipitate of ferrous sulfide, FeS, is obtained from basic solutions. The precipitate turns brown upon exposure to air.

$$Fe^{++} + H_2S + 2\,H_2O \rightleftharpoons \underset{\text{Black}}{FeS\downarrow} + 2\,H_3O^{+}$$

The precipitate is soluble in acids giving off hydrogen sulfide.

3. Ferrocyanide ion, $Fe(CN)_6^{3-}$ solution (use $K_4Fe(CN)_6$ sol.)

If the reaction between this reagent and the ferrous ion is carried out in complete absence of air, a white precipitate of potassium ferrous ferrocyanide, $K_2[Fe(Fe(CN)_6]$, is formed. However, partial oxidation by atmospheric oxygen may take place, which in turn produces a light blue mixture of potassium ferric ferrocyanide $KFe(Fe(CN)_6]$.

$$Fe^{++} + 4\ K^{+} + Fe(CN)_6^{3-} \rightleftharpoons \underset{\text{White}}{K_2[Fe(Fe(CN)_6]} + 2K^{+}$$

If potassium ferricyanide, $K_3[Fe(CN)_6]$, solution is used a dark blue precipitate is obtained.

$$Fe^{++} + 3\ K^{+} + Fe(CN)_6^{3-} \rightleftharpoons \underset{\text{Deep blue}}{KFe(Fe(CN)_6} + 2K^{+}$$

In a basic solution, hydrogen sulfide or ammonium sulfide solution gives a black precipitate of ferric sulfide, Fe_2S_3

$$2\ Fe^{++} + 3\ S^{=} \rightleftharpoons \underset{\text{Black ppt.}}{Fe_2S_3}$$

The blue precipitate turns reddish brown if sodium or potassium hydroxide solution is added to it, causing the decomposition of the precipitate and the formation of $Fe(OH)_3$.

E. Identification of the Cobaltous ion, Co^{++}

A list of some of the insoluble cobaltuse compounds is given in table 13 below:

Table 13 Insoluble cobaltuse compounds with their colors

Compound	color
↓ CoC_2O_4	Raddish white
* $Co(OH)_2$	Rose-red
$CoCO_3$	Red
CoS	Black

* Decreasing Concentration of Co^{++} Ion

1. Aqueous ammonia

A blue basic precipitate, $Co(OH)NO_3$ is formed when aqueous ammonia is added to a solution of cobaltous nitrate.

$$Co^{++} + NO_3^{-} + NH_3\ \text{aq.} + H_2O \rightleftharpoons \underset{\text{Black}}{Co(OH)NO_3}\downarrow + NH_4^{+}$$

$Co(OH)NO_3$ is readily dissolves in excess of aqueous ammonia, due to the formation of the cobaltose ammonia complex ion, $Co(NH_3)_6^{++}$.

$$Co(OH)NO_3 + 6\ NH_3\ \text{aq.} \rightleftharpoons Co(NH_3)_6^{++} + NO_3^{-} + OH^{-}$$

2. Alkali hydroxide solutions.

A pink precipitate of cobaltose hydroxide, $Co(OH)_2$ is formed in the presence of slight excess NaOH solution. $Co(OH)_2$ is soluble in excess of the alkali hydroxide, if the concentration of the hydroxide ions is higher than 8 molar.

$$Co^{++} + 2\ OH^{-} \rightleftharpoons \underset{\text{Pink}}{Co(OH)_2}\downarrow$$

$$Co(OH)_2 + 2\ OH^{-} \rightleftharpoons CoO_2^{=} + 2H_2O$$

Exposure of $Co(OH)_2$ to atmospheric oxygen leads to the formation of brown cabaltic hydroxide, $Co(OH)_3$.

Addition of H_2O_2 or Na_2O_2 in a high concentration of the hydroxide ions converts $Co(OH)_2$ to $Co(OH)_3$ very rapidly.

$$2\ Co(OH)_2 + O_2 + 2\ H_2O \rightleftharpoons \underset{\text{Brown}}{2Co(OH)_3} + 2OH^-$$

3. Sulfide ion solution (H_2S or $(NH_4)_2S$)

In a neutral or basic solution with ammonia, the sulfide ion combines with the cobaltuse ion to form a black precipitate of cobaltose sulfide, CoS.

$$Co^{++} + H_2S + 2\ H_2O \rightleftharpoons \underset{\text{Black ppt.}}{CoS} + 2\ H_3O^+$$

Cobaltose sulfide in insoluble in a very dilute acids and in acetic acid, but dissolved readily by concentration HCl, HNO_3 and by aqua regia. In the case of HCl, CoS dissolves quite slowly.

$$CoS + 2\ H_3O^+ \rightleftharpoons Co^{++} + H_2S + 2\ H_2O$$

$$CoS + 4\ H_3O^+ + 2\ NO_3^- \rightleftharpoons Co^{++} + 2\ NO_2 + S + 6\ H_2O$$

4. Thiocyanate ion

when an alcoholic solution of NH_4CNS is added slowly to the surface of a slightly acidic solution containing Co^{++} ions without mixing, an intense blue color is formed, because of the formation of the cobalti thiocyanate complex ion, $Co(CNS)_4^{=}$ the color appears at the junction of the two liquids.

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

Mixing or diluting the solution, containing $Co(CNS)_4^{=}$ ions, with water destroys this complex ion.

The same test may be performed in a different way, by adding concentrated NH_4CNS solution then extracting the blue complex ions of $Co(CNS)_4^{=}$ by shaking with amyl alcohol.

F. Identification of the Nickelous ion, Ni^{++}

A list of some of the insoluble nickelous compounds is given in table 14 below:

Table 14 Insoluble nickelous compounds with their colors

Compound		color
	$Ni(IO_3)_2$	Yellow
*	$NiCO_3$	Light green
	$Ni(OH)_2$	Green
	$Ni(CN)_2$	Green
↓	NiS	Black

* Decreasing Concentration of Ni^{++} Ion

1. Alkali hydroxide solutions.

A solution of NaOH. For example, precipitates the light green gelatinous nickelous hydroxide, $Ni(OH)_2$ from solutions of Ni^{++} ion.

$$Ni^{++} \quad + \quad 2 \rightleftharpoons OH^- \downarrow \quad Ni(OH)_2$$

Light green ppt.

$Ni(OH)_2$ is soluble un solutions containing NH_3 or NH_4^+ ions producing a grennish blue solutions of the complex ions, $Ni(NH_3)_4^{++}$ and $Ni(NH_3)_6^{++}$

$$Ni(OH)_2 + 4\ NH_3\ aq. \rightleftharpoons Ni(NH_3)_4^{++} + 2\ OH^-$$
$$Ni(OH)_2 + 6\ NH_3\ aq. \rightleftharpoons Ni(NH_3)_6^{++} + 2\ OH^-$$

$Ni(NH_3)_6^{++}$ is more stable (K_{inst}= 1.8 x 10^{-9}) than $Ni(NH_3)_4^{++}$ (K_{inst}= 1.0 x 10^{-8}).

2. Aqueous ammonia

A green basic precipitate is formed upon the addition of aqueous ammonia to a solution of nickelous chloride.

$$Ni^{++} + Cl^- + NH_3\ aq. + H_2O \rightleftharpoons NiOHCl\downarrow + NH_4^+$$

Green ppt.

NiOHCl is soluble in excess of aqueous ammonia, due to the formation of the complex ion, $Ni(NH_3)_6^{++}$.

$$NiOHCl + 7\ NH_3\ aq. + H_2O \rightleftharpoons Ni(NH_3)_6^{++} + NH_4^+ + Cl^- + 2\ OH^-$$

Violate-blue

3. Sulfide ion solution (H_2S or $(NH_4)_2S$)

In basic solutions, the sulfide ion combines with the nickelous ion to form a black precipitate of nickelous sulfide, NiS.

$$Ni^{++} + H_2S + 2\ H_2O \rightleftharpoons NiS + 2H_3O^+$$

Black

The hydronium ions formed are removed from the solution through the reaction with base NH_3 in the solution, giving NH_4^+ ions. In other words the reaction may be written as follows:-

$$Ni^{++} + H_2S + 2\ NH_3\ aq. \rightleftharpoons NiS + 2\ NH_4^+$$

4. Dimethylglglyoxime, $C_4H_8O_2N_2$ solution

When an alcoholic solution of dimethylglyoxime is added to a slightly ammoniacal solution (basic with ammonia) containing Ni^{++} ions, a red precipitate of nickel dimethylglyoxime, $Ni(C_4H_7O_2N_2)_2$ is formed.

$$Ni^{++} + 2\ C_4H_8O_2N_2 + 2\ NH_3\ aq. \rightleftharpoons Ni(C_4H_7O_2N_2)_2 + 2\ NH_4^+$$

Red ppt.

G. Identification of the Manganous ion, Mn^{++}

A list of some of the insoluble Manganous compounds is given in table 15 below:

Table 15 Insoluble manganous compounds with their colors

	Compound	color
↓	$Mn(OH)_2$	White pink
	$MnCO_3$	Rose-pink
*	MnS	Green or pink
	$MnSO_4$	white

* Decreasing Concentration of Mn^{++} Ion

1. Hydroxide ion solution

a. Aqueous ammonia

Manganous ions are partially precipitated by aqueous ammonia, as white manganous hydroxide, $Mn(OH)_2$.

$$Mn^{++} + 2\ NH_3 + 2\ H_2O \rightleftharpoons \underset{\text{White}}{Mn(OH)_2}\downarrow + 2NH_4^+$$

The precipitate is soluble in solutions containing as appreciable amount of NH_4^+ ions, since the latter upon hydrolysis furnishs H_3O^+ ions which will neutralize the OH^- ions, thereby reducing the OH^- ions in solution which are in equilibrium with $Mn(OH)_2$.

b. Alkali hydroxide solutions .

Addition of NaOH solution, for example, to a solution containing Mn^{++} ions results in the complete precipitating of white manganous hydroxide, $Mn(OH)_2$

$$Mn^{++} + 2\ OH^- \rightleftharpoons \underset{\text{White}}{Mn(OH)_2}\downarrow$$

The precipitate is insoluble in excess of the precipitant. Exposure of $Mn(OH)_2$ to the air results in the conversion of the precipitate to the brown manganic hydroxide, $Mn(OH)_3$ or the hydrated dioxide, $MnO_2 .xH_2O$.

$$4\ Mn(OH)_2 + O_2 + 2\ H_2O \rightleftharpoons \underset{\text{Brown ppt.}}{4\ Mn(OH)_3}\downarrow$$

Manganous ion, in the presence of Na_2O_2 and excess NaOH produces a brown precipitate of the hydrated manganese dioxide.

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

$$4\ Mn(OH)_2 + O_2^= + H_2O \rightleftharpoons \underset{\text{Brown}}{MnO(OH)_2} + 2OH^-$$

or, $$Mn(OH)_2 + O_2^= + xH_2O \rightleftharpoons \underset{\text{Brown}}{MnO_2 .xH_2O} + 2OH^-$$

3. Sulfide ion solution (H_2S or $(NH_4)_2S$ sol.)

In a slightly basic solutions, manganous ion gives a light pink precipitate of, manganous sulfide when reacts with the sulfide ion.

$$Mn^{++} + H_2S + 2\ NH_3\ aq. \rightleftharpoons \underset{\text{Pink}}{MnS}\downarrow + 2\ NH_4^+$$

Mns is soluble in dilute acids and in acetic acid this is because MnS is not very insoluble, thus it furnishes a relatively high concentration of the sulfide ions that are removed by the formation of HS^- ion and H_2S.

4. Bismuthate ion solution (use $NaBiO_3$).

Manganous ions, in a cold solution containing dilute nitric acid are oxidized by the bismuthate ions (usually added as solid $NaBiO_3$) to the reddish purple or violet-red permanganate ions NnO_4^-.

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

High concentration of the Mn^{++} ion may produce dark solution, but the color can be clearly noticed after filtering off the excess of solid bismuthate and then diluting the filtrate with water.

Several other oxidizing agents may be used for the oxidation of Mn^{++} ion to MnO_4^- ion, such as PbO_2, $(NH_4)S_2O_8$ and KIO_4 but with different procedures.

H. Identification of the Zinc ion, Zn^{++}

A list of some of the insoluble zinc compounds is given in table 16 below:

Table 16 Insoluble zinc compounds with their colors

Compound	color
* ↓ $Zn(CN)_2$	White
ZnC_2O_4	White
$ZnSO_3$	White
$Zn_2Fe(CN)_6$	White
$Zn(OH)_2$	White
ZnS	White

* Decreasing Concentration of Zn^{++} Ion

1. Hydroxide ion solution

a. Aqueous ammonia

A white precipitate of zinc hydroxide, $Zn(OH)_2$ is formed upon the addition of aqueous ammonia, to a solution of zinc ion.

$$Zn^{++} + 2\ NH_3\ aq. + 2\ H_2O \rightleftharpoons \underset{\text{White}}{Zn(OH)_2\downarrow} + 2\ NH_4^+$$

$$Zn(OH)_2 + 4\ NH_3\ aq. \rightleftharpoons Zn(NH_3)_4^{++} + 2\ OH^-$$

b. Alkali hydroxide solutions .

Zinc ion reacts with the alkali solution giving a white gelatinous precipitate of zinc hydroxide, $Zn(OH)_2$

$$Zn^{++} + 2\ OH^- \rightleftharpoons \underset{\text{White}}{Zn(OH)_2\downarrow}$$

$Zn(OH)_2$ is soluble in excess of the precipitant,

$$Zn(OH)_2 + OH^- \rightleftharpoons Zn(OH)_3^-$$

or, $$Zn(OH)_2 + 2\ OH^- \rightleftharpoons ZnO_2^{=} + 2H_2O$$

And also soluble in dilute acids,

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

3. Sulfide ion solution (H_2S or $(NH_4)_2S$)

In a basic solutions, zinc ion gives a white precipitate of, zinc sulfide (ZnS) when reacts with the sulfide ion in aqueous ammonia solution.

$$Zn^{++} + H_2S + NH_3\ aq. \rightleftharpoons \underset{\text{White}}{ZnS\downarrow} + 2\ NH_4^+$$

Partial precipitation, as sulfide, take place in neutral or very slightly acidic solutions. If the ammoniacal solution of Zn^{++} ions is acidified with acetic acidic can then saturated with H_2S, the precipitate of ZnS will be formed.

$$Zn(NH_3)_4^{++} + 4\ HC_2H_3O_2 \rightleftharpoons Zn^{++} + 4\ NH_4^+ + 4\ C_2H_3O_2^-$$

$$Zn^{++} + H_2S + 2\ H_2O \rightleftharpoons \underset{\text{White ppt.}}{ZnS} + 2H_3O^+$$

ZnS is insoluble in excess of the precipitant, in acetic acid and in alkali solutions, but readily dissolves in mineral acids.

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

4. 8-quinolinol solution.

Zinc ion and 8-quinolinolate react with each other, in a solution saturated with ammonium acetate to give a light yellow precipitate of zinc 8-quinolinolate $Zn(C_9H_6NO)_2$.

$$Zn^{++} + 2\ C_9H_6NOH + 4\ H_2O \rightleftharpoons \underset{\text{Yellow}}{Zn(C_9H_6NO)_2.2H_2O\downarrow} + 2H_3O^+$$

The principle of the separation of group III

It was mentioned that the chlorides and sulfides of group III cations are soluble in acid media, otherwise they would precipitate with either the members of group I or II or may be with both.

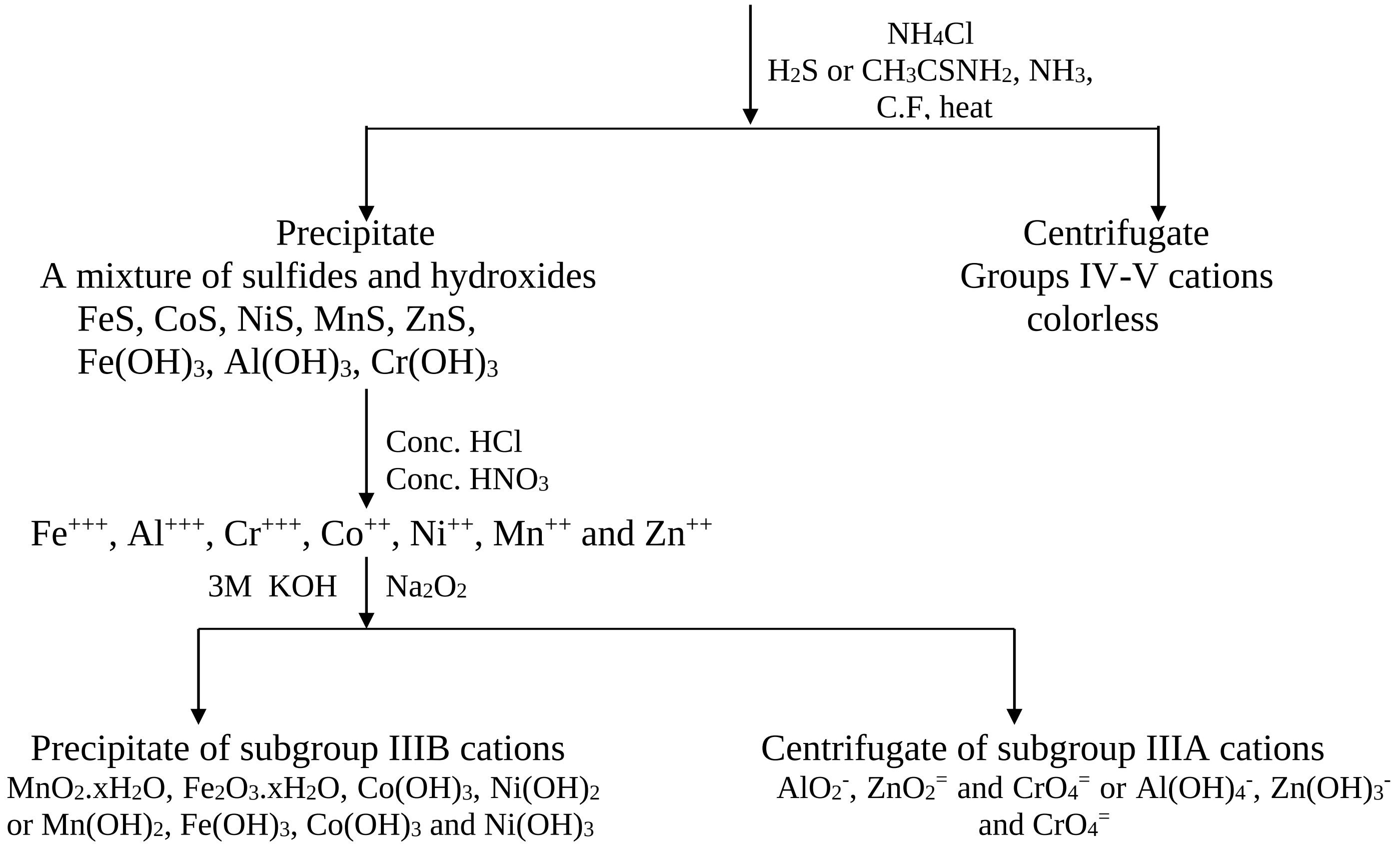
The separation of group III cations from groups IV and V is based upon the fact that the sulfides and hydroxides of this group are insoluble in moderately ammoniacal solution, while those of group IV and V are soluble.

Fairly complete precipitation of the members of this group is usually made in an ammoniacal solution buffered with NH_4Cl using both the sulfide and hydroxide ions as the precipitants. The presence of NH_3 in the solution has two functions. First, it will precipitate the hydroxides (or rather the hydrous oxides) of Al, Cr and Fe, and second it will increase the concentration of the sulfide ions to a value that permits the solubility product constants of ZnS, FeS, NiS, CoS and MnS to be exceeded.

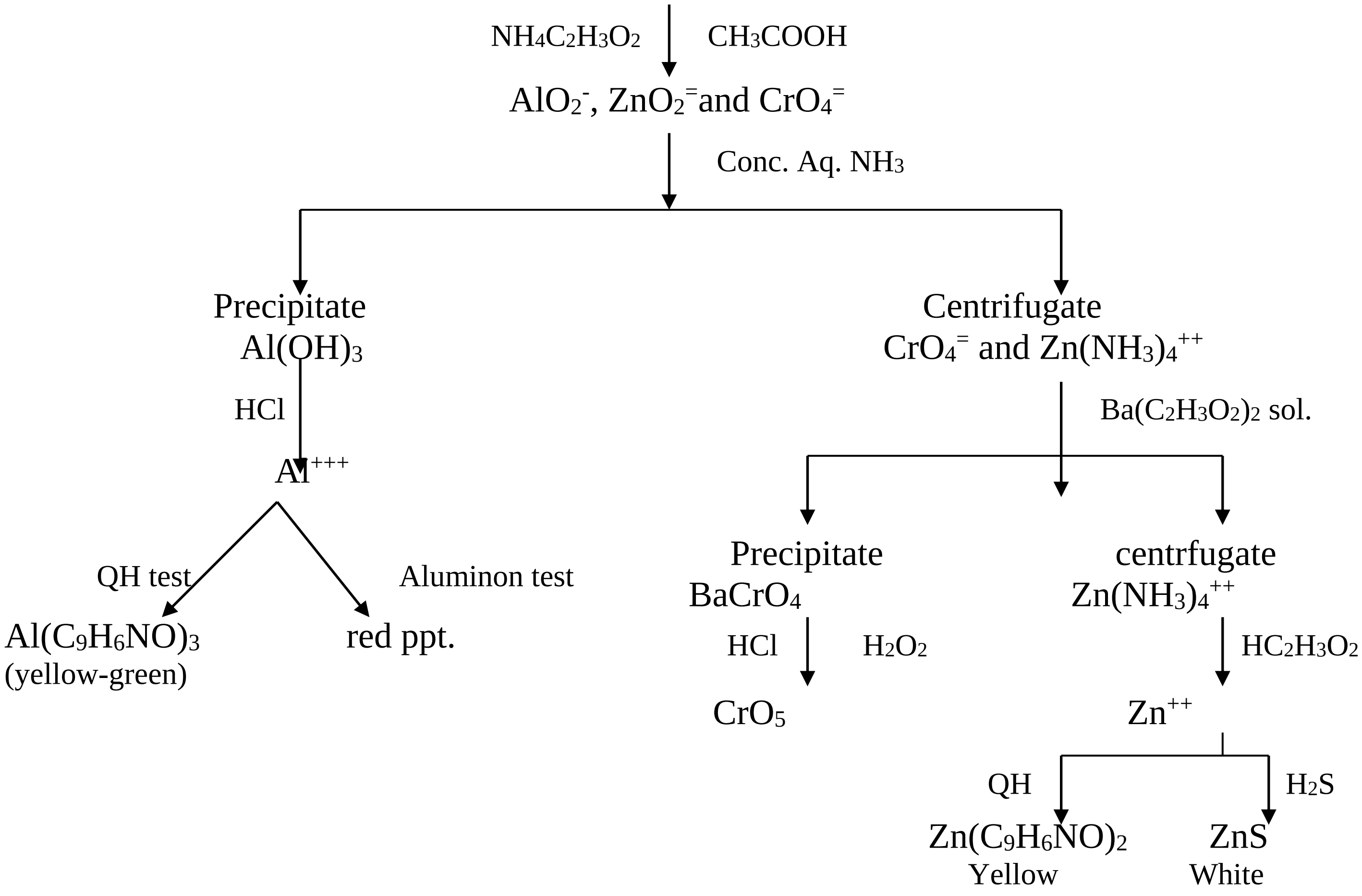
The hydroxide ion concentration must be sufficiently high to precipitate the above hydroxides, and to increase the sulfide ion concentration so that the above cations are precipitated. But it should not be so high as to case the precipitation of magnesium ion (a member of group IV cations) as magnesium hydroxide, $Mg(OH)_2$.

The insoluble hydroxides and sulfides of group III cations are soluble is concentrated hydrochloric acid, with exception of CoS and NiS which are soluble in concentrated HNO_3. when dissolution is complete, the group can then be divided into two subgroups, by the action of excess KOH or NaOH solution and Na_2O_2. Subgroup IIIA will include aluminum, chromium and zinc ions. At the step of separation into the two subgroups, these three cations will be present as the aluminate , AlO_2^-, zincate, $ZnO_2^=$, and chromate, $CrO_4^=$ ions whereas the ferric, manganous, cobaltic and nickelous ions are precipitated as their corresponding hydroxides to form subgroup IIIB.

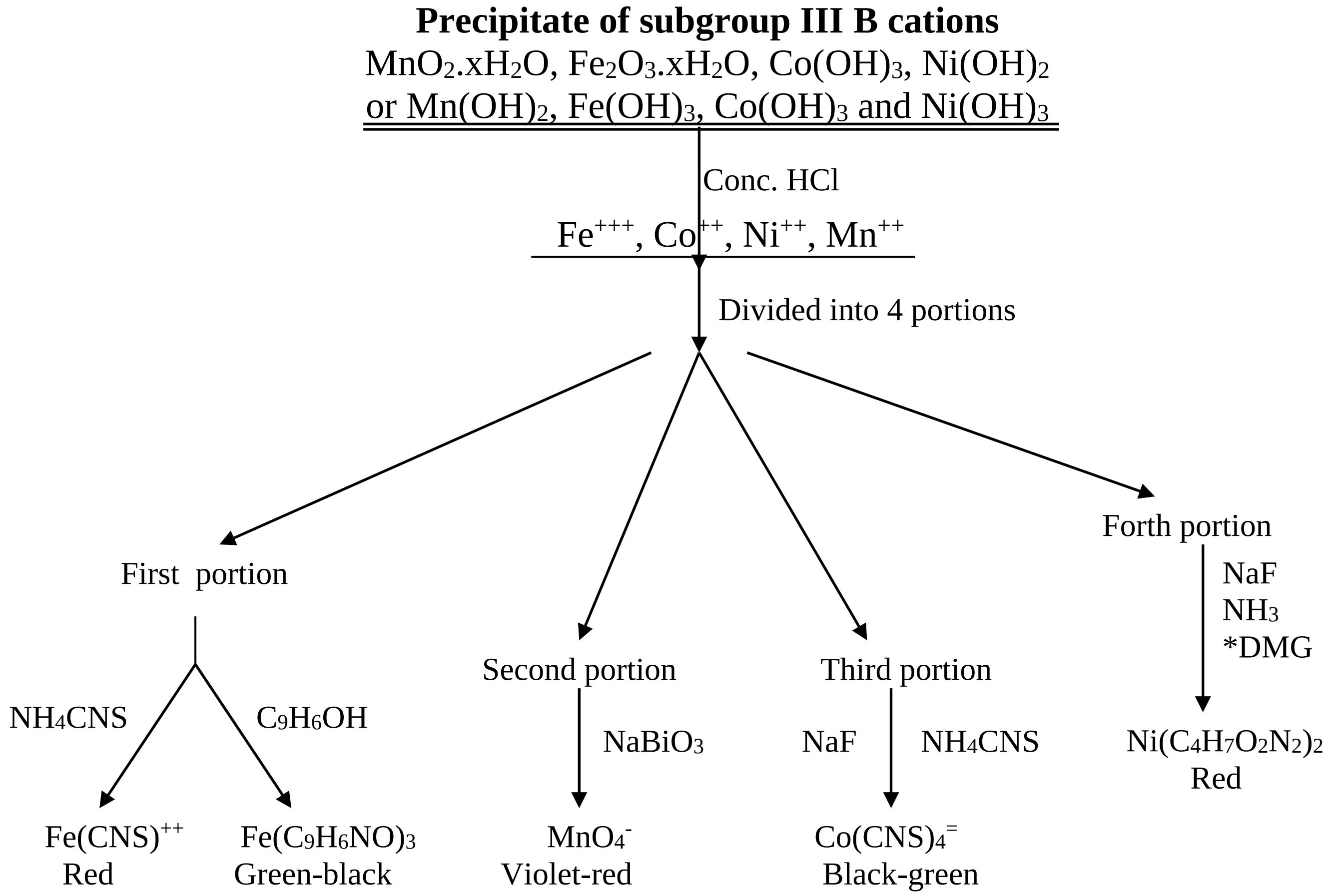
Group III-IV and V cations



Analysis of subgroup III A cations



Analysis of subgroup III B cations



* DMG = dimethylglyoxime = $C_4H_8O_2N_2$

Procedure NO. 3 Analysis of Group III cations

<table>
<tr><td colspan="2">Precipitation of the group:
The centrifugate (from group II, procedure No.2), may contain any or all the cations of groups III. IV and V. adjust the volume of the centrifugate 1 ml. Add 4 drops of saturated NH_4Cl solution then concentrated NH_3 (1) solution drop by drop until the solution is just basic. Add 1 ml of the bases and pass H_2S until precipitation is complete centrifuge.</td></tr>
<tr><td>Precipitate:
Contains FeS (b), CoS (b), NiS (b), MnS (p), ZnS (w), $Al(OH)_3$ (w), $Fe(OH)_3$ (r-br), $Cr(OH)_3$ (gr-grn). Wash twice with water and discard washing. Treat the ppt. with 5 drop of concentrated HCl.
Stir thoroughly for about a minute. If the ppt. dissolves completely, Ni and Co must be absent (3). Add 3 drops of concentrated HNO_3 and heat until the precipitate dissolves. Make the solution basic with 3M KOH sol. then , slowly and carefully, add 0.2 gram of Na_2O_2 (4), (5). Heat for a few minutes and centrifuge. Wash the residue with 10 drops of water and combine washing with centrifuge.</td><td>Centrifugate
Contains groups IV and V Acidify immediately with hydrochloric acid and boil (2) to 1 ml , discarding any ppt. which may form reserve the colorless sol. for the analysis of groups IV and V cations.</td></tr>
<tr><td>Precipitate of subgroup IIIB cations
Contains $MnO_2.xH_2O$, $Co(OH)_3$, $Ni(OH)_2$ and $Fe(OH)_3$. Wash with 10 drops of water treat according to procedure No. 2</td><td>Centrifugate (subgroup IIIA cations)
Contains AlO_2^-, $ZnO_2^=$, and $CrO_4^=$ ions. Treat according to procedure No.1</td></tr>
</table>

Nots on procedure :

1. Aqueous ammonia precipitates some of the cations as hydroxides or oxides, and also neutralizes the hydronium ions which are used by the reaction of the cations with H_2S. for example:

$$Co^{++} + H_2S + 2H_2O \longrightarrow CoS + 2H_3O^+$$

$$NH_3 + H_3O^+ \longrightarrow NH_4^+ + H_2O$$

In the solution is not kept basic, complete precipitation may be prevented. Ammonia and ammonium chloride from a buffer solution which represses the OH^- ion concentration to certain values at which $Mg(OH)_2$ cannot be precipitated.

2. Unless the sulfide ion is removed from the solution by acidifying and boiling ,

$$S^= + 2H_3O^+ \longrightarrow H_2S + 2H_2O$$

It will be oxidized to the sulfate ion by the atmospheric oxygen.

$$S^= + 2O_2 \longrightarrow SO_4^=$$

The formed $SO_4^=$ ion may cause a loss of some cations of group IV such as Sr^{++} and Ba^{++} because of the formation of $SrSO_4$ and $BaSO_4$ which are both insoluble.

3. Concentrated HCl, readily dissolves $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$, FeS, MnS and ZnS but very slowly the precipitate of CoS and NiS. A black ppt. after the addition of concentrated hydrochloric acid which dissolves in concentrated HNO_3 may indicate any or both, CoS and NiS.

4. A large excess of Na_2O_2 in a strongly alkaline solution may partially disperce $Fe(OH)_3$, $Co(OH)_3$ and $Ni(OH)_2$ which in turn affect the test for Al^{+++} and Zn^{+++} ions.

5. sodium peroxide, Na_2O_2 , oxidizes the chromic ion, Cr^{++}, in the presence of KOH of NaOH to the chromate ion, $CrO_4^=$, $Fe(OH)_2$ to $Fe(OH)_3$ and $Co(OH)_2$ to $Co(OH)_3$.

Procedure NO. 1 Analysis of subgroup III A cations

Centrifugeate, (from procedure of subgroup IIIA cations) The centrifugate contain AlO_2^-, $ZnO_2^=$, and $CrO_4^=$ ions. Add 10 drops of saturated ammonium acetate solu. Then add drop by drop of acetic acid solution until the test solution becomes acidity and then add aqueous ammonia until the solution becomes ammoniacal. Then centrifugate.	
Precipitate: May contain gelatinous white ppt. $Al(OH)_3$, wash with 10 drops water, then add 3M HCl drop by drop until the ppt. disappeared, add 3 drops of saturated	Centrifugate May contain $Zn(NH_3)_4^{++}$ and $CrO_4^=$ add dropwise 1M of barium acetate $Ba(C_2H_3O_2)_2$ solution until precipitation is complete. Then centrifuge.

ammonium acetate solution and divided into two unequal parts. Large porting: Add 2-3 drops of aluminon solution then render basic with 3M of aq. ammonia. Formation of red ppt. confirms presence of Al^{+++} ion. Smaller part: Make the solution almost neutral with 3M aq. ammonia, then add 5 drops of 8-quinolinol solution. Formation of a greenish yellow ppt. which is little soluble in acetone or ethanol and highly fluorescent, confirms presence of Al^{+++} ion.	Precipitate, $BaSO_4$ (1) $BaCrO_4$ (y), add 10 drops of HCl and warm for 1 min. in a Water bath. Centrifuge and discard the white ppt. ($BaSO_4$). Add 10 drops of amyl alcohol and 5 drops of H_2O_2 and shake well. A blue upper layer (2) containing CrO_5 confirms presence of Cr^{+++} ion.	Centrifugate, Contains $Zn(NH_3)_4^{++}$ acidify with 3M CH_3COOH and divided into two unequal parts: Large porting: Saturate with H_2S and warm in a water bath for few minutes, a white ppt. of ZnS confirms presence of Zn^{++} ion. If the ppt. is not white (3) or fails to form, use then the smaller part. Smaller part: Add 3 drops of saturated ammonium acetate solution then add 4 drops of 8-quinolinol solution. Yellow ppt. of $Zn(C_9H_6NO)_2$ insoluble in acetone or ethanol it confirms Zn^{++} ion.

Nots on procedure :

1. Na_2O_2 oxidizes any $S^{=}$ ions in the solutions to $SO_4^{=}$ ions. The sulfate ions will precipitate as $BaSO_4$ when barium acetate solution is added.
2. the blue coloration, due to CrO_5, may not last long since CrO_5 is unstable , decomposing with the evaluation of oxygen gas.
3. the precipitate of ZnS may not be white but brown or black due to contamination with CoS or PbS. Lead sulfide, PbS, is formed here after some of the lead ions have escaped from group II cations.

Procedure NO. 2 Analysis of subgroup IIIB cations

Precipitate:, (from procedure of subgroup IIIB cations) May contain MnO_2xH_2O, $Ni(OH)_2$, $Co(OH)_3$ and $Fe(OH)_3$. wash with 10 drops of water and discard washings. Dissolve in concentrated hydrochloric acid then dilute with water to about 2ml divided equally into four portions.			
1 st. portion **Test for Fe^{+++}**	**2 nd. Portion** **Test for Mn^{++}**	**3ed. Portion** **Test for Co^{++}**	**4 th. Portion** **Test for Ni^{++}**

Divided into two parts a and b Part a. Add 2 drops of 3M NH_4CNS sol. deep red coloration proves presence of Fe^{+++}. Part b. Make solution almost neutral with 3M aqueous ammonia, then add 3 drops of 8-quinolinol solution. Deep greenish–black coloration, or fine precipitate (1) proves presence of Fe^{+++} ion	Add 0.2 gram of $NaBiO_3$ and shake well for a minute, then centrifuge, reddish-purple centrifugate , MnO_4^- ion proves presence of Mn^{++} ion.	Add with stirring enough solid NaF (2) that undissolved amount remains. Carefully let 10 drops alcoholic NH_4CNS sol(3) , rundown side of the test tube containing the test solution. Formation of a blue-green ring proves presence of Co^{++} ion.	Add with stirring enough solid NaF (2) that undissolved amount remains. Add 3M aq. ammonia drop by drop until the solution is slightly basic. Add 4 drops of dimethylglyoxime sol. formation of a red precipitate proves presence of Ni^{++} ion (4).

Nots on procedure :

1. if only a greenish-black coloration appears, one can get the precipitate by saturating the solution with ammonium acetate.
2. Any amount of ferric ions must be removed, since Fe^{+++} ions interfere with the test for cobalt and nickel ions. The addition of NaF results in the formation of the stable and colorless ion, FeF_6^{---} which dose not react with either CNS^- ions or dimethylglyoxime.
3. The blue-cobaltothiocyanate complex ion, $Co(CNS)_4^{=}$, is stable in alcoholic solution but not in aqueous solution. It may be destroyed during the addition of alcoholic thiocyanate solution, if the test solution is shaken or stirred.
4. in the presence of cobaltouse ions, which also react with dimethylglyoxime to form a dark colored complex ions, one should add an excess of the precipitant to ensure the formation of nickel dimethylglyoximate, $Ni(C_4H_7N_2O_2)_2$.

Report sheet

Analysis of group IIIcations

Name:……………………………… Unknown No.:……………………..

Section:……………………………. Date:……………………………….

Notes and Equations :

Ions of group III	*Ions found, by the student*	*Ions present in the unknown solution*	*grade*
Al^{+++} **Cr**$^{+++}$ **Fe**$^{+++}$ **Co**$^{++}$ **Ni**$^{++}$ **Mn**$^{++}$ **Zn**$^{++}$			

Signature of the student Signature of the grader

Group IV
The Alkaline Earth Group
Ba^{++}, Sr^{++}, Ca^{++} and Mg^{++} ions

This group is composed of the ions of the alkaline earth metals and magnesium. The chlorides, sulfides and hydroxides of those cations are soluble under the conditions of the precipitations of the first three groups of the cations. These ions are characterized by the formation of a relatively large number of insoluble salts, with various anions, but the only anion which will precipitate these four cations satisfactorily is the phosphate anion.

Due to the fact that the metals of these cations are included in the same group of the periodic table, they have the same valence and resemble each other closely in their chemical reactions. These cations are also known to be excellent reducing agents, do not hydrolyze and show little tendency toward complex formation.

A . Identification of the Barium ion, Ba^{++}

A list of some of the insoluble barium compounds is given in table 17

Table 17 Insoluble barium compounds with their colors

Compound	**color**
BaF_2	White
* $BaSO_3$	White
BaC_2O_4	White
↓ $Ba(IO_3)_2$	White
$BaCO_3$	White
$BaCrO_4$	Yellow
$BaSO_4$	White
$Ba_3(PO_4)_2$	White

* Decreasing Concentration of Ba^{++} Ion

1. Phosphate ion solution (use $(NH_4)_2HPO_4$).

Diammonium acid phosphate solution precipitates barium ions, from ammoniacal solution as a white gelatinous precipitate of barium phosphate, $Ba_3(PO_4)_2$.

$$Ba^{++} + 2HPO_4^{=} + 2NH_3\,\text{aq.} \rightleftharpoons \underset{\text{White ppt.}}{Ba_3(PO_4)_2}\downarrow + 2NH_4^{+}$$

$Ba_3(PO_4)_2$ is soluble in mineral acids, and in the absence of large excess of the acetate ions, barium phosphate is also soluble on acetic acid.

$$Ba_3(PO_4)_2 + 4CH_3COOH \rightleftharpoons 3Ba^{++} + 2H_2PO_4^{-} + 4CH_3COO^{-}$$

2. Sulfate ion solution (use H_2SO_4)

The sulfate ion precipitates the barium ion as a white finely divided precipitate of barium sulfate, $BaSO_4$.

$$Ba^{++} + SO_4^{=} \rightleftharpoons \underset{\text{White ppt.}}{BaSO_4\downarrow}$$

$BaSO_4$ is insoluble in dilute acids, but can be dissolved by boiling with concentrated sulfuric acid where the bisulfate ion, HSO_4^- is formed.

$$BaSO_4 + 2H_3O^+ + SO_4^{=} \rightleftharpoons Ba^{++} + 2\,HSO_4^- + 2H_2O$$

3. Chromate ion solution (use K_2CrO_4 or Na_2CrO_4 sol.)

The chromate ion precipitates the barium ion as a yellow precipitate of barium chromate, $BaCrO_4$.

$$Ba^{++} + CrO_4^{=} \rightleftharpoons \underset{\text{Yellow ppt.}}{BaCrO_4\downarrow}$$

$BaCrO_4$ is soluble in mineral acids, but insoluble in acetic acid (distinction from $SrCrO_4$ and $CaCrO_4$).

$$2BaCrO_4 + 16H_3O^+ + 6Cl^- \rightleftharpoons 2Ba^{++} + 2Cr^{+++} + 3Cl_2 + 24H_2O$$

4. Flame test:

Barium salts, especially the chloride, impart a yellow green color to the flame when heated in Bunsen flame. Clean the platinum wire by dipping it into concentrated hydrochloric acid and then heating it in the hottest oxidizing of the flame. Repeat this process until any color disappears the loop of the Pt wire in the solution being tested and then heat in the oxidizing zone of the flame. A yellowish-green coloration of the flame confirms presence of barium ion.

B . Identification of the Strontium ion, Sr^{++}

A list of some of the insoluble strontium compounds is given in table 18

Table 18 Insoluble strontium compounds with their colors

	Compound	color
	$Sr(OH)_2$	White
*	$SrCrO_4$	Yellow
	SrF_2	White
	$SrSO_4$	White
	SrC_2O_4	White
	$SrCO_3$	White
↓	$Sr_3(PO_4)_2$	White

* Decreasing Concentration of Sr^{++} Ion

1. Phosphate ion solution (use $(NH_4)_2HPO_4$).

Diammonium acid phosphate solution precipitates strontium ions, from ammoniacal solution as a white gelatinous precipitate of strontium phosphate, $Sr_3(PO_4)_2$.

$$3Sr^{++} + 2HPO_4^{=} + 2NH_3aq. \rightleftharpoons \underset{\text{White ppt.}}{Sr_3(PO_4)_2\downarrow} + 2NH_4^{+}$$

$Sr_3(PO_4)_2$ is soluble in mineral acids, and in the absence of large excess of the acetate ions are absent.

$$Sr_3(PO_4)_2 + 4CH_3COOH \rightleftharpoons 3Sr^{++} + 2H_2PO_4^{-} + 4CH_3COO^{-}$$

2. Sulfate ion solution (use H_2SO_4)

The sulfate ion reacts with the strontium ion to product a white precipitate of strontium sulfate, $SrSO_4$.

$$Sr^{++} + SO_4^{=} \rightleftharpoons \underset{\text{White ppt.}}{SrSO_4\downarrow}$$

$SrSO_4$ slightly soluble in boiling hydrochloric acids, but sufficiently soluble to give a flame test for the strontium ion.

3. Carbonate ion solution (use $(NH_4)_2CO_3$ or Na_2CO_3 sol.)

The carbonate ion precipitates from slightly basic solutions the strontium ion as a white precipitate of strontium carbonate, $SrCO_3$.

$$Sr^{++} + CO_3^{=} \rightleftharpoons \underset{\text{White ppt.}}{SrCO_3\downarrow}$$

$SrCO_3$ is soluble in mineral acids, acetic acid and in water saturated with carbone dioxide.

$$SrCO_3 + H_2O + CO_2 \rightleftharpoons Sr^{++} + 2HCO_3^{-}$$

4. Flame test:

Strontium salts, especially the chloride, when heated in Bunsen flame. Import a characteristic crimson (brilliant red) color to the flame.

C . Identification of the Calcium ion, Ca^{++}

A list of some of the insoluble Calcium compounds is given in table 19

Table 19 Insoluble calcium compounds with their colors

Compound	color
↓ $CaCrO_4$	Yellow
$Ca(OH)_2$	White
* $CaSO_4$	White
CaF_2	White
$CaSO_3.2H_2O$	White
$CaCO_3$	White
CaC_2O_4	White
$Ca_3(PO_4)_2$	White

* Decreasing Concentration of Ca^{++} Ion

1. Phosphate ion solution (use $(NH_4)_2HPO_4$).

Diammonium acid phosphate solution precipitates calcium ions, from ammoniacal solution as a white gelatinous precipitate of calcium phosphate, $Ca_3(PO_4)_2$.

$$3Ca^{++} + 2HPO_4^{=} + 2NH_3 \text{ aq.} \rightleftharpoons \underset{\text{White ppt.}}{Ca_3(PO_4)_2\downarrow} + 2NH_4^{+}$$

$Ca_3(PO_4)_2$ is soluble in mineral acids, and in the absence of large excess of the acetate ions, it dissolves in acetic acid too.

$$Ca_3(PO_4)_2 + 4CH_3COOH \rightleftharpoons 3Ca^{++} + 2H_2PO_4^{-} + 4CH_3COO^{-}$$

2. Carbonate ion solution (use $(NH_4)_2CO_3$ or Na_2CO_3 sol.)

The carbonate ion precipitates from slightly basic solution the calcium ion as a white precipitate of calcium carbonate, $CaCO_3$.

$$Ca^{++} + CO_3^{=} \rightleftharpoons \underset{\text{White ppt.}}{CaCO_3\downarrow}$$

$CaCO_3$ is soluble in mineral acids, acetic acid and in a saturated aqueous solution with carbone dioxide.

$$CaCO_3 + 2H_3O^{+} \rightleftharpoons Ca^{++} + 3H_2O + CO_2$$
$$CaCO_3 + 2H_2O + CO_2 \rightleftharpoons Ca^{++} + 2HCO_3^{-}$$

3. Oxalate ion solution. (use $(NH_4)_2C_2O_4$ sol.)

In ammoniacal solution, the oxalate ion, $C_2O_4^{=}$, reacts with the calcium ion to form a white precipitate of calcium oxalate, $CaC_2O_4 . H_2O$.

$$Ca^{++} + C_2O_4^{=} \rightleftharpoons \underset{\text{White ppt.}}{CaC_2O_4\downarrow}$$

4. Flame test:

Calcium salts, especially the chloride, import when heated in bunsen flame. Import a brick-red color to the flame.

D . Identification of the Magnesium ion, Mg^{++}

A list of some of the insoluble Mg^{++} compounds is given in table 20

Table 20 Insoluble Magnesium compounds with their colors

Compound	color
MgC_2O_4	White
* $MgCO_3$	White
MgF_2	White
$Mg_3(PO_4)_2$	White
$Mg(OH)_2$	White
↓ $MgNH_4PO_4$	White

* Decreasing Concentration of Mg^{++} Ion

1. Phosphate ion solution (use $(NH_4)_2HPO_4$).

In an ammoniacal solution containing ammonium chloride, magnesium ion reacts with $HPO_4^{=}$ ion producing a white crystalline precipitates of magnesium ammonium phosphate $MgNH_4PO_4.6H_2O$.

$$3Mg^{++} + HPO_4^{=} + NH_3\text{ aq.} + 6H_2O \rightleftharpoons \underset{\text{White ppt.}}{MgNH_4PO_4.6H_2O}\downarrow$$

$MgNH_4PO_4.6H_2O$ is soluble in mineral acids, and also in acetic acid too.

$$MgNH_4PO_4.6H_2O + 2CH_3COOH \rightleftharpoons Mg^{++} + 2H_2PO_4^{-} + 2CH_3COO^{-} + NH_4^{+}$$

2. Aqueous ammonia

Aqueous ammonia precipitates magnesium ions, from solutions containing no ammonia salts, as a white precipitate of magnesium hydroxide, $Mg(OH)_2$.

$$Mg^{++} + 2NH_3\text{ aq.} + 2H_2O \rightleftharpoons \underset{\text{White ppt.}}{Mg(OH)_2}\downarrow + 2NH_4^{+}$$

The precipitate is readily soluble in acids and in aqueous solutions of ammonia salts.

3. Magneson I (p-nitrobenzeneazoresorcinol) solutrion.

Sodium or potassium hydroxide precipitates magnesium ion as magnesium hydroxide, $Mg(OH)_2$

$$Mg^{++} + 2OH^{-} \rightleftharpoons \underset{\text{White ppt.}}{Mg(OH)_2}\downarrow$$

Magneson I, p-nitrobenzeneazoresorcinol, is an organic dye which can be adsorbed by $Mg(OH)_2$ in a strongly alkaline solution producing a blue precipitate, or rather a blue lake. Other cations of group IV do not interfere in this test.

The principle of separation

It was previously mentioned that the alkaline earth metals and magnesium are included within one group of the periodic table. Thus, they resemble each other closely in their reactions, especially barium, strontium and calcium. This characteristic of close chemical relationship makes it very difficult to obtain a clean separation of these three cations from each other by precipitation methods. This difficulty arises from the fact that any precipitant chosen may bring down all the three cations as precipitates having close values of solubility product constants.

To establish a clean separation between two or more ions using one precipitant, the ratio between the two solubility product of at least one million to one. The ratio of the solubility product constants of any two carbonate or oxalate salts of the last table, is not of the order that permits fairy quantitative separation. Therefore, and because Ca^{++}, Sr^{++} and Ba^{++} ions show characteristic colors of the flame, the flame test which is more specific should be employed.

Slightly soluble carbonate and oxalate salts of group IV cations with their solubility product constants values.

Salt	Ks.p	Salt	Ks.p
$MgCO_3$	1.0×10^{-5}	MgC_2O_4	8.6×10^{-5}
$CaCO_3$	8.7×10^{-9}	CaC_2O_4	2.3×10^{-9}
$SrCO_3$	1.6×10^{-9}	SrC_2O_4	5.8×10^{-8}
$BaCO_3$	8.1×10^{-9}	BaC_2O_4	1.5×10^{-7}

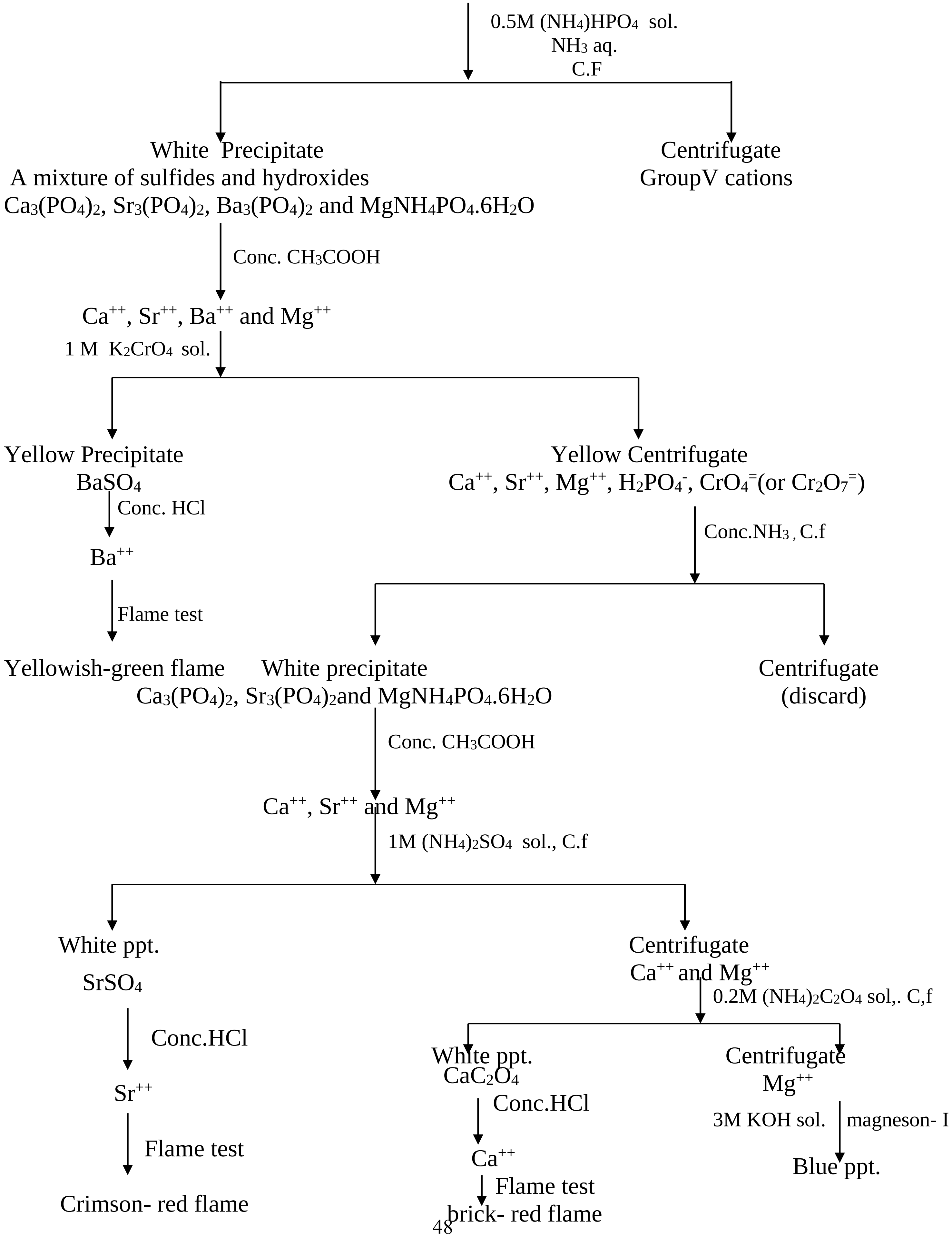
Although several anions can precipitate four members of group IV cations, only the phosphate anion is capable of accomplishing satisfactory precipitation.

For the separation of group IV cations from group V cations, two general methods are known to be used. In the first method, the carbonate anion, $CO_3^{=}$, is employed as the group precipitant. In this case, the Mg^{++} ion becomes a member of group V cations scince it dose not precipitate as carbonate. In the second method, the phosphate anion is the precipitate agent for group IV cations.

The precipitation with the phosphate ion takes place in a strongly ammoniacal solution where the calcium, strontium and barium ions are precipitated as the tertiary phosphate while magnesium ion is precipitated as magnesium ammonium phosphate.

Analysis of group IV

Filtrate of group IV and V cations



Procedure NO. 4 Analysis of Group IV cations

Precipitation of the group: The centrifugate (from group III, procedure No.3), may contain any or all the cations of groups IV and V. Adjust the volume to 1 ml discarding any precipitate that may form add 10 drops 0f 0.5M $(NH_4)_2HPO_4$ solution and render strongly basic with concentrated aqueous ammonia. Allow the mixture to stand for a few minutes, test for complete precipitation then centrifuge .

Precipitate: Contains $Ca_3(PO_4)_2$, $Sr_3(PO_4)_2$and $MgNH_4PO_4.6H_2O$ wash with 5drops of water and discard washings. Add upon the precipitate 5 drops of concentrated CH_3COOH, and stir thoroughly. Any undissolved precipitate will prove by dissolve upon the dilution. Dilute the solution to 2 ml, then add 5 drops of 1M K_2CrO_4 sol. and stir for a minute centrifuge and test for complete pptn.	Centrifugate Contains groupV cations.

Precipitate May contain $BaCrO_4$ (y). wash with hot water until washings became colorless. Add 5 drops of conc. HCl stir and heat then apply the flame test, a yellowish-green flame confirms Ba^{++} ion.	Centrifugate Contains Ca^{++}, Sr^{++}, Mg^{++} $H_2PO_4^-$ and $CrO_4^=$ ions. Add conc. Aqueous ammonia until the solution is strongly ammoniacal, then centrifuge.

Precipitate May contains $Ca_3(PO_4)_2$, $Sr_3(PO_4)_2$and $MgNH_4PO_4.6H_2O$. dissolve in conc. Acetic acid, as above and dilute to 1 ml, add 5 drops 0f 0.1M $(NH_4)_2HPO_4$ solution and heat to boiling. Test for complete precipitation then cool and centrifuge.	Centrifugate CrO_4 ions Discard

Precipitate May be $SrSO_4$ (w). treat with 3 drops of conc. HCl stir and heat then apply the flame test, a crimson-red flame confirms Sr^{++} ion.	Centrifugate May contain Ca^{++} and Mg^{++} ions. add 5 drops 0f 0.2M $(NH_4)_2HPO_4$ solution and heat to boiling. Test for complete precipitation then cool and centrifuge.

Precipitate May be CaC_2O_4 (w). treat with 2 drops of conc. HCl stir and heat then apply the flame test, a brick-red flame confirms Ca^{++} ion.	Centrifugate May contain Mg^{++} ions. Add 2 drops of magneson I sol. then 3 ml of 3M KOH sol. heat for a few minutes and centrifuge. Wash with 2 ml of KOH solution or water a blue ppt. confirms Mg^{++} ion

Report sheet

Analysis of group IVcations

Name:……………………………… Unknown No.:……………………..

Section:……………………………. Date:……………………………….

Notes and Equations :

Ions of group IV	***Ions found, by the student***	***Ions present in the unknown solution***	***grade***
Ca^{++} Sr^{++} Ba^{++} Mg^{++}			

Signature of the student Signature of the grader

Group V Cations

The alkaline metals group
Na^+, K^+ and NH_4^+ ions

This group, which may be called soluble group of the cations, is composed of lithium, sodium, potassium and ammonium ions. However, lithium ion will not be included in this manual since it is, known to be a less common compared with sodium and potassium ions.

The alkali metals are the most strongly electropositive elements known, hence they are highly reactive and can not exist in ear as free metals due to the rapid reaction with oxygen and moisture, they always tend to attention their stability by losing their outermost shell electron to became ion of +1 oxidation state. They are also characterized by the formation of salts, which a few exceptions, are quite soluble in water.

Ammonium ion, NH_4^+, shows similar properties to those of the alkali metals, such as having a charge of +1, forming salts the majority of which are water soluble and is not precipitated in the previous four groups.

There is no precipitating agent for this group, and identification of each ion is performed in the presence of the other.

A. Identification of the Sodium ion Na^+

A list of some of the slightly soluble sodium salts is given in table 21 below:

Table 21 slightly soluble sodium salts with their colors and molar solubilities

Compound	color	Molar solubility
Na_2SiF_6	White	0.035
$Na_2H_2Sb_2O_7$	White	0.008

1. Flame test:

Sodium salts, especially the chloride, when heated in bunsen flame. Impart an intense yellow color to the flame.

B. Identification of the Potasium ion K^+

A list of some of the slightly soluble potasium salts is given in table 22 below:

Table 22 slightly soluble potasium salts with their colors and molar solubilities

Compound	color	Molar solubility
$KClO_4$	White	0.15
K_2PtCl_6	Yellow	0.03
K_2SiF_6	White	0.006
$K2CO(NO_2)_6$	White	0.001

1. Flame test:

Potassium salts, especially the chloride, when heated in bunsen flame. Impart a pale violate color to the flame. If sodium ions are present, the intense yellow flame of sodium will mask the violate color of potassium flame. Therefore, it will be necessary to view through a filter of two thickness cobalt glass which will absorb the yellow sodium rays leaving only a visible reddish-violate color of the potassium rays.

C. Identification of the Ammonium ion NH_4^+

A list of some of the slightly soluble ammonium salts is given in table 23 below:

Table 23 slightly soluble ammonium salts with their colors and molar solubilities

Compound	**color**	**Molar solubility**
$NH_4HC_4H_4O_6$	White	0.06
$(NH_4)_2PtCl_6$	Yellow	0.01
$(NH_4)_2CO(NO_2)_6$	Yellow	0.001

1. Alkali hydroxide solution.
   Addition of sodium or potassium hydroxide solution to a solution containing ammonium ions liberates ammonia gas, NH_3, which can be driven out easily upon gentle heating.

$$NH_4^+ + NaOH \rightleftharpoons NH_3\uparrow + H_2O + Na^+$$

The librated ammonium can be identified by its odor or by its action upon a wet red litmus paper, held at the mouth of the test tube which will turn blue due to the formation of OH^- ions. Another sensitive method is the development of a black color on a filter paper wetted with mercurous nitrate solution, when held on the mouth of the test tube that gives of NH_3 gas.

$$Hg_2^{++} + NO_3^- + 2NH_3\,aq. \rightleftharpoons \underset{\text{Black}}{HgNH_2NO_3 + Hg} + NH_4^+$$

2. Nessler's reagent (sol. of K_2HgI_4 +NaOH)

The addition of Nessler's reagent solution containinh ammonium ions or ammonia produce a brown-red colloidal precipitate or coloration ranging from yellow to brown depending upon the amount of ammonia, or the amount of the ammonium ions present in the solution.

$$2HgI_4^= + NH_3aq. + OH^- \rightleftharpoons \underset{\text{Brown-red}}{NH_2Hg_2I_3} + H_2O + 5I^-$$

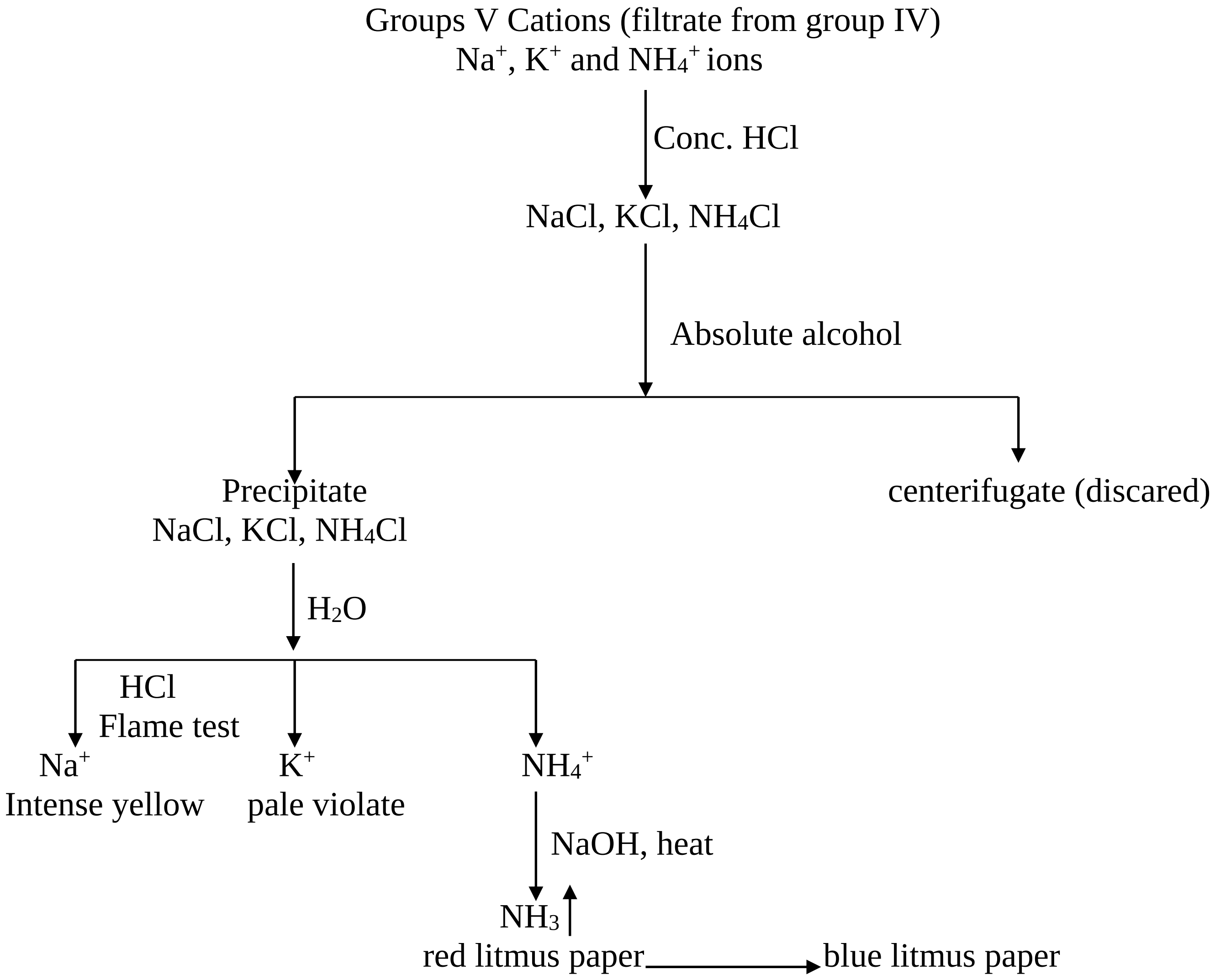
The principle of separation

It is well understood now that the metal ions (cations) of group V are not precipitated with the cations of the earlier groups. In other words, their chlorides, sulfides, hydroxides and phosphate salts are soluble under the conditions of the precipitation by the early group reagents. For this reason , group V is sometimes called the soluble group of the cations.

The test for the NH_4^+ ion most be made on a portion of the original solution, otherwise the test for this cation in group V will always be positive, regardless of its presence in the original solution or not. The test for NH_4^+ ion in group V is meaningless since solutionof ammonia or ammonium salts are added several times throughout the group separation. The identification of the ammonium ion by the addition of KOH or NaOH solution is very simple and sensitive, and the evolved NH_3 gas can be recognized by several methods.

Sodium and potassium ions can be identified, in the presence of each other, by means of precipitations reactions. However, the interference of several cations with these tests necessitate the use of the flame test which is more reliable method for the confirmation of Na^+ and K^+ ions than that of precipitations method.

Analysis of group V cations



Report sheet

Analysis of group V cations

Name:……………………………… Unknown No.:……………………..

Section:……………………………. Date:……………………………….

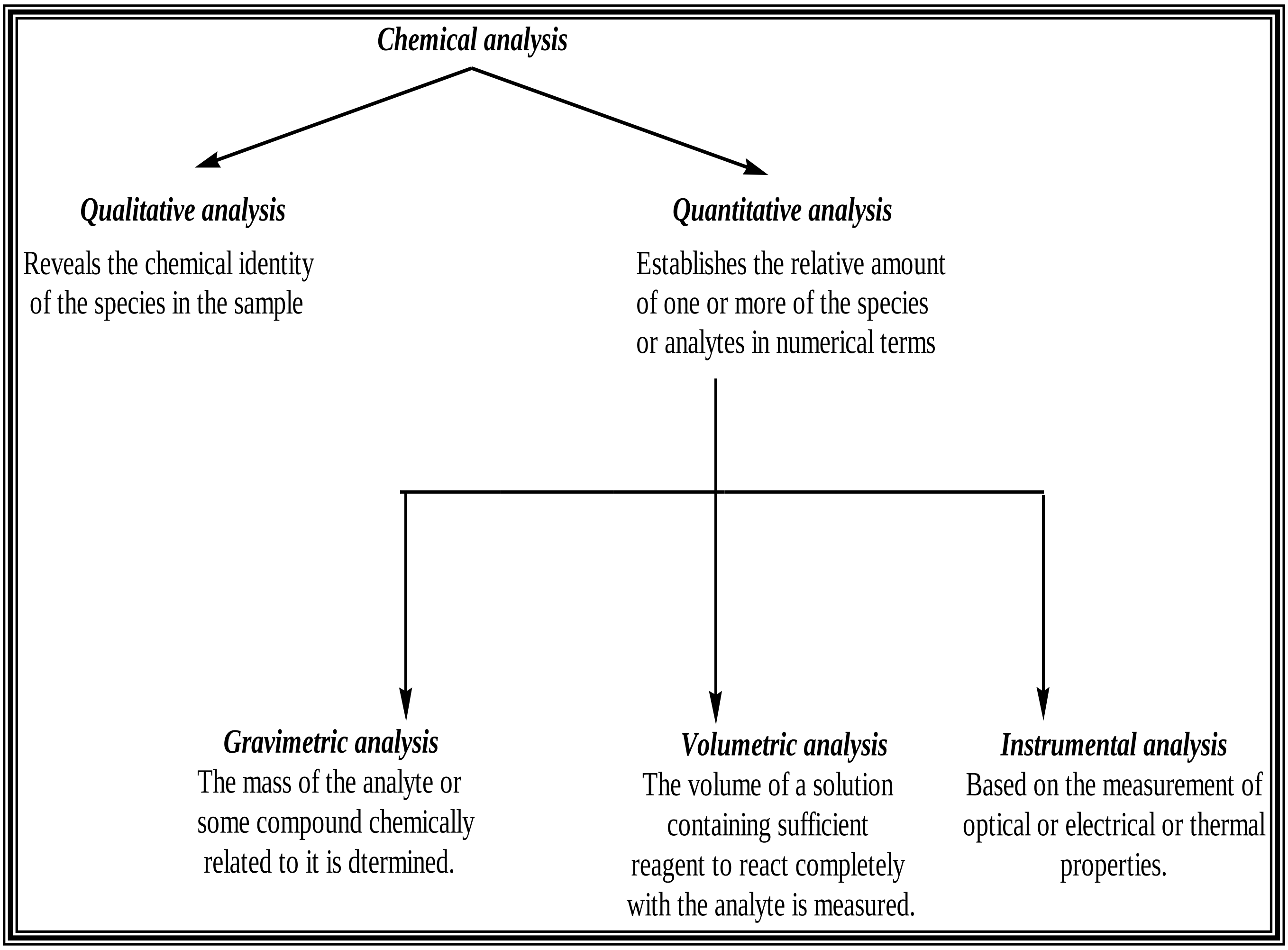
Notes and Equations :

Ions of group V	***Ions found, by the student***	***Ions present in the unknown solution***	***grade***
Na^+ K^+ NH_4^+			

Signature of the student Signature of the grader

Analytical chemistry

is the science of the characterization and measurement of chemicals and also involve separating ,identifying and determining the relative amounts of the components in a sample of matter.Chemical analysis is divided into two types ***Quantitative analysis*** and ***Qualitative analysis .***



Qualitative analysis
Reveals the chemical identity of the species in the sample

Quantitative analysis
Establishes the relative amount of one or more of the species or analytes in numerical terms

Gravimetric analysis
The mass of the analyte or some compound chemically related to it is dtermined.

Volumetric analysis
The volume of a solution containing sufficient reagent to react completely with the analyte is measured.

Instrumental analysis
Based on the measurement of optical or electrical or thermal properties.

Volumetric analysis

Volumetric analysis is a general term for a method in quantitative chemical analysis in which the amount of a substance is determined by the measurement of the volume that the substance occupies. It is commonly used to determine the unknown concentration of a known reactant. Volumetric analysis is often referred to as **titration**.

What is the meaning of Titration?

Titration is a common laboratory method of quantitative chemical analysis that is used to determine the unknown concentration of a known reactant. Because volume measurements play a key role in titration, it is also known as *volumetric analysis*.

A reagent, called the *titrant* or *titrator*,[1] of a known concentration (a standard solution) and volume is used to react with a solution of the analyte or *titrand*,[2] whose concentration is not known. Using a calibrated burette or chemistry pipetting syringe to add the titrant.

*** A primary standard solution** is a highly purified compound that serve as a reference material in all volumetric titrimetric methods.

Important requirements for a primary standard are :

1-High purify.
2-Stability toward air.
3-Absence of hydrate water.
4-Ready availability at modest cost.
5-Reasonable solubility in the titration medium.
6-Reasonable large molar mass so that the relative error associated with weighing the standard is minimized.

It is possible to determine the exact amount that has been consumed when the *endpoint* is reached. The **endpoint** is the point at which the titration is complete, as determined by an indicator. This is ideally the same volume as the **equivalence point**—the volume of added titrant at which the number of moles of titrant is equal to the number of moles of analyte.

For example:- in the classic strong acid-strong base titration, the endpoint of a titration is the point at which the pH of the reactant is just about equal to 7, and often when the solution takes on a persisting solid color as in the pink of phenolphthalein indicator. There are however many different types of titrations.

Many methods can be used to indicate the endpoint of a reaction; titrations often use visual indicators (the reactant mixture changes color). In simple acid-base titrations a pH indicator may be used, such as phenolphthalein, which becomes pink when a certain pH (about 8.2) is reached or exceeded. Another example is methyl orange, which is red in acids and yellow in alkali solutions.

Not every titration requires an indicator. In some cases, either the reactants or the products are strongly colored and can serve as the "indicator". For example, a redox titration using potassium permanganate (pink/purple) as the titrant does not require an indicator. When the titrant is reduced, it turns colorless. After the equivalence point, there is excess titrant present. The equivalence point is identified from the first faint persisting pink color (due to an excess of permanganate) in the solution being titrated.

Types of titrations

There are various sorts of titrations whose goals are different to the others. The most common types of titrations in qualitative work are acid-base titrations ,redox titrations, complexometric titration and precipitation titration.

1- Acid-base titration

These titrations are based on the neutralization reaction that occurs between an acid and a base, when mixed in solution. The acid is added to a burette which was rinsed with the same acid prior to this addition to prevent contamination or diluting of the acid being measured. The base is added to a volumetric flask which had been rinsed with distilled water prior to the addition to prevent contamination or dilution of the base/alkali being measured. The solution in the volumetric flask is often a standard solution(one whose concentration is exactly known). The solution in the burette, however, is the solution whose concentration is to be determined by titration. The indicator used for such an acid-base titration often depends on the nature of the constituents. Common indicators, their colours, and the pH range in which they change colour, are given in the table below, when more precise results are required, or when the titration constituents are a weak acid and a weak base, a pH meter or a conductance meter are used.

Indicator	**Color on Acidic Side**	**Range of Color Change**	**Color on Basic Side**
Methyl Violet	Yellow	0.0 - 1.6	Violet
Bromophenol Blue	Yellow	3.0 - 4.6	Blue
Methyl Orange	Red	3.1 - 4.4	Yellow
Methyl Red	Red	4.4 - 6.2	Yellow
Litmus	Red	5.0 - 8.0	Blue
Bromothymol Blue	Yellow	6.0 - 7.6	Blue
Phenolphthalein	Colorless	8.3 - 10.0	Pink
Alizarin Yellow	Yellow	10.1 - 12.0	Red

2- Precipitation titration

Precipitation titration :is titration depend upon the combination of ions to form a simple precipitate. Mohr method is a method depend upon formation a colored precipitate for the determination of chloride ion.

A small quantity of potassium chromate (K_2CrO_4) solution is added to serve as indicator. The first excess of titrant results in the formation of a red silver chromate precipitate which signal the end point.

3-Redox titration

These titrations are based on a redox reaction between an oxidizing agent and a reducing agent. The oxidizing agent is added to the burette which was rinsed with the same oxidizing agent. The reducing agent is added to the conical flask, which had been rinsed with distilled water. Like in an acid-base titration, the standard solution is often the one in the conical flask, and the solution whose concentration is to be determined is the one in the burette.

Some redox titrations do not require an indicator, due to the intense colour of some of the constituents. For instance, in a titration where the oxidizing agent potassium permanganate (permanganometry) is present, a slight faint persisting pink colour signals the endpoint of the titration, and no particular indicator is therefore required.

4- Complexometric titration

These titrations are based on the formation of a complex between the analyte and the titrant. The chelating agent EDTA is very commonly used to titrate metal ions in solution. These titrations generally require specialized indicators that form weaker complexes with the analyte. A common example is Eriochrome Black T and muroxide for the titration of calcium and magnesium ions.

Titrimetric analysis generally involve the following steps:

- Sampling
- Titrant preparation
- Standard preparation and conversion to a measurable form
- Titrant standardization by titration of an accurately know quantity of standard
- Sample preparation and conversion to a measurable form
- Sample titration with the titrant solution
- Data analysis

Successful Titrimetric Analysis

A few rules of thumb for designing a successful titration are:

- The titrant should either be a standard or should be standardized.
- The reaction should proceed to a stable and well defined equivalence point.
- The equivalence point must be able to be detected.
- The titrant's and sample's volume or mass must be accurately known.

- The reaction must proceed by a definite chemistry. There should be complicating side reactions.
- The reaction should be nearly complete at the equivalence point. In other words, chemical equilibrium favors products.
- The reaction rate should be fast enough to be practical.
- Substances of known purity for the preparation of standard solution.
- A visual indicator or an instrumental method detecting the completion of the reaction
- Calibrated measuring vessels, including burettes, pipettes, and measuring flasks as followes:-


Burette


Erlenmeyer flask


Volumetric flask

Calculations of volumetric analysis:

Standard solution is one, which contains a known weight of the reagent in a definite volume of the solution.
Molar solution is one, which contains 1 gm molecular weight of the reagent per liter of solution.

$$\boxed{M= \frac{\text{Weight}}{\text{M.Wt}} * \frac{1000}{\text{Volume(mL)}}}$$

Normal solution is one that contains 1gm equivalent weight per liter of solution.

$$\boxed{N= \frac{\text{Weight}}{\text{eq.wt}} * \frac{1000}{\text{Volume(mL)}}}$$

Part per million(ppm): Milligrams of solute per liter of solution.

$$\boxed{\mathbf{ppm=\frac{weight\ solute(mg)}{Volume\ solution(L)}}}$$

$$\mathbf{ppm = \frac{wt(g)}{V(mL)} \times 10^6}$$

$$\mathbf{ppm = M\times M.wt\times 1000}$$

……………………………………………………………………

For titrimetric reaction:

$$\underset{\text{titrant}}{a\,A} + \underset{\text{titrand}}{b\,B} \rightarrow \text{product}$$

At equivalent point:

no.mmol of titrant(A)= no.mmol of titrand(B)

$$N_A \times V_A = N_B \times V_B$$

or $$M_A \times V_A \times R = M_B \times V_B \qquad (R=b/a)$$

Equivalent weights

(1)Equivalent weight in neutralization reactions.

The equivalent weight of acid is that weight of it which contains one-gram atom of replaceable hydrogen.

Ex: **equivalent weight of H_2SO_4 =M.Wt $H_2SO_4/2$**
equivalent weight of H_3PO_4 =M.Wt $H_3PO_4/3$

$$\boxed{\text{eq.wt acid} = \frac{\text{M.Wt acid}}{\text{No. of active }H^+}}$$

The equivalent weight of Base is that weight of it which contains one replaceable hydroxyl group.

Ex: **equivalent weight of NaOH =M.Wt NaOH/1**

$$\boxed{\text{eq.wt base} = \frac{\text{M.Wt base}}{\text{No. of active }OH^-}}$$

(2)Equivalent weight in Oxidation -reduction reactions.

The equivalent weight of an oxidant or a reductant is the number of electrons which 1moL of the substance gains or loses in the reaction.

$$\boxed{\text{eq.wt} = \frac{\text{Formula weight (gm/mole)}}{\text{No. of lost or gained electrons}}}$$

Ex:

$$5C_2O_4^{=}+2MnO_4^{-} +16H^{+} \rightarrow 10\,CO_2+2Mn^{2+} +8H_2O$$

$$\text{eq.wt } MnO_4^{-} = \frac{\text{F.wt } MnO_4^{-}}{5} \qquad \text{eq.wt } C_2O_4^{=} = \frac{\text{F.wt } C_2O_4^{=}}{2}$$

(3) Equivalent weight of complex formation and precipitation reactions.

Here the equivalent weight is the weight of the substance which *contains* or *reacts* with 1g. atm of a univalent cation M^+.

Ex: When silver nitrate reacts with sodium chloride, to form silver chloride, the equivalent weight of $AgNO_3$ is:

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3 \qquad \text{eq.wt }(AgNO_3)= \frac{\text{F.wt } AgNO_3}{1}$$

……

Experiment (1)

A: Preparation of approximately (0.1N) HCl

1-Calculate the normality of the concentrated HCl :

$$\boxed{N=\frac{Sp.g * \text{Percentage} * 1000}{\text{equivalent weight}}}$$

$$N=\frac{1.19 * (37/100) * 1000}{36.5} \quad =12.0630$$

2-To prepare (500mL) of 0.1N HCl :

$$\underset{\text{conc.HCl}}{N_1 \times V_1} = \underset{\text{dil.HCl}}{N_2 \times V_2}$$

$$12.0630 \times V_1 = 500 \times 0.1$$

$$V_1 = 4.1449 \text{ mL}$$

Transfer distilled water to a glass-Stoppard bottle and add about 4.14 ml of conc. HCl Mix the contents of the bottle thoroughly. Dilute to the mark with distilled water and make a label.

B: Preparation of (0.1N) sodium carbonate:

1-Dry a quantity of primary-standard sodium carbonate for 2 hours at 110 °C, cool in a desiccator .Weigh 1.325gm of the salt into a small beaker, and dissolve in 25 to 50 mL of distilled water.

2-Transfer this solution to a 250mL volumetric flask. Wash the beaker and transfer this washing water to the volumetric flask. Dilute to the mark with distilled water and mix thoroughly. Make a label.

$$\boxed{N=\frac{\text{Weight}}{\text{equivalent weight}} * \frac{1000}{\text{Volume(mL)}}}$$

Experiment (2)

Standardization of HCl solution with standard solution of Na_2CO_3

1-Clean the burette and rinse with HCl solution.
2-Fill the burette with HCl.
3-Pipet 10 ml of standard solution (Na_2CO_3) into a 250mL conical flask. Add 3 drops of Methyl orange indicator.
4-Titrate by adding HCl drop wise until the solution just beings to change from yellow to red.
5-Reapeat the titration a few times until you gets approximate results. Take the average of the results and subtract 0.05mL. (This result represents the volume of extra drop which change the color of indicator.
6-Calculate the normality of HCl :

$$N_{acid} \times V_{acid} = N_{base} \times V_{base}$$

7-Make label on your bottle containing your name, date of preparation and concentration of acid after standardization .
8- The equation of reaction :

$$Na_2CO_3 + HCl \xrightarrow{M.O} H_2CO_3 + 2NaCl$$

Experiment (3)

Analysis of sodium carbonate Na_2CO_3

1-Clean the burette and rinse with standardized HCl solution and then fill it with the acid.
2-Pipet 10 ml unknown solution (Na_2CO_3) into a 250mL conical flask . Add 2 drops of phenolphthalein indicator the solution will be pink.
3-Titrate by adding HCl drop wise until the solution just beings to change its color from pink to coloreless this data will be (V1).
4- Add 1-2 drops of Methyl orange indicator to the above solution which became yellow then complete the titration until the color of the solution became pale orange (onion), this data will be (V2).
5-Reapeat the titration a twice time until you gets approximate results. Take the average of the results and subtract 0.05mL. (This result represents the volume of extra drop which change the color of indicator.

6- Make a table as bellow:-

	First titration	**Second titration**	**Third titration**	**Average of titrations**
Titration with ph.ph	**V1**	**V1**	**V1**	**V1 (av.)**

Titration with M.O	**V2**	**V2**	**V2**	**V2 (av.)**

$$\textbf{V1(av.)} = \frac{V1+V1+V1}{3}$$

V1(av.) =1/2 $CO_3^{=}$
V2(av.) = 1/2 $CO_3^{=}$
V1+V2 = $V_{tot.}$ of Na_2CO_3

$$\mathbf{N_{acid} \times V_{(tot.)\ acid\ (from\ burette)} = N_{base} \times V_{base}}$$

7- The equation of reaction :

$$Na_2CO_3 + HCl \xrightarrow{ph.ph} NaHCO_3 + NaCl$$

Pink colorless

$$NaHCO_3 + HCl \xrightarrow{M.O} H_2CO_3 + NaCl$$

Yellow pale orange

Experiment (4)

Analysis of a mixture (sodium hydroxide + sodium carbonate)

1-Transfer a (10ml) of a mixture solution to 250 ml conical flask and add 1drop of phenolphthalein indicator.
2-Clean the burette and rinse with hydrochloric acid.
3-Fill the burette with HCl.
4-Titrate with standard hydrochloric acid solution until the pink color disappears (the solution will be colorless).
* At this stage: all the hydroxide and half the carbonate have been neutralized. Let us assume that the volume of acid be "X" ml.
5-Now add 3drops of Methyl Orange indicator into the solution above and continue the titration until the solution just begins to change from yellow to red.
* At this stage :another half of carbonate has been neutralized. Let the volume of acid be "Y" ml.
6-Repeat the titration a few times until you get approximate results.

Calculations:

(X-Y)=Z → Volume of HCl which equivalent to OH^- …………….(1)
2×Y→Volume of HCl which equivalent to $CO_3^{=}$…… ……………(2)

$$\mathbf{N_{acid} \times V_{acid} = N_{base} \times V_{base}}$$
$$\mathbf{N_{acid} \times Z = N_{OH^-} \times 10 \quad …….. (1)}$$
$$\mathbf{N_{acid} \times 2Y = N\ CO_3^{=} \times 10 \quad …….. (2)}$$

Concentration of $[OH^-]_{(ppm)} = N_{OH^-} \times$ eq.wt ×1000

Concentration of $[CO_3^{=}]_{(ppm)}$= N $CO_3^{=}$ × eq.wt ×1000

……………………………………………………………………

Experiment (5)

Analysis of a mixture (sodium bicarbonate + sodium carbonate)

1-Repeat the same steps of the experiment no.3.
2-Volume of acid at the end point of Ph.Ph indicator=X.
3-Volume of acid at the end point of M.O indicator=Y.
X=Volume of HCl≡1/2 $CO_3^{=}$
Y=Volume of HCl≡1/2 $CO_3^{=}$ + HCO_3^{-}

(Y-X)=Z → Volume of HCl which equivalent to HCO_3^{-} …………….(1)
2×X→Volume of HCl which equivalent to $CO_3^{=}$…… ……………(2)

$N_{acid} \times V_{acid} = N_{base} \times V_{base}$
$N_{acid} \times Z = N\, HCO_3^{-} \times 10$ …….. (1)
$N_{acid} \times 2X = N\, CO_3^{=} \times 10$ …….. (2)

Concentration of $[HCO_3^{-}]_{(ppm)}$= N HCO_3^{-} × eq.wt ×1000
Concentration of $[CO_3^{=}]_{(ppm)}$ = N $CO_3^{=}$ × eq.wt ×1000

…………………………………………………………………………………

Experiment (6)

Determination of chloride ion by Mohr method

Precipitation titration :is titration depend upon the combination of ions to form a simple precipitate. Mohr method is a method depend upon formation a colored precipitate for the determination of chloride ion.

Chloride ion ,is reacted with silver nitrate solution to form AgCl precipitate.

$$AgNO_3 + NaCl \Leftrightarrow AgCl + NaNO_3 \qquad Ksp_{AgCl} = 1.2\times10^{-10}$$

A small quantity of potassium chromate (K_2CrO_4) solution is added to serve as indicator. The first excess of titrant results in the formation of a red silver chromate precipitate which signal the end point.

$$2AgNO_3 + K_2CrO_4 \Leftrightarrow Ag_2CrO_4 + 2KNO_3 \qquad Ksp_{Ag2CrO4} = 1.7\times10^{-12}$$

Procedure:

1-Clean the burette and fill it with silver nitrate(0.1N).
2-Pipet 10mL of chloride ion solution into 250mL conical flask, add 5drops of potassium chromate.
3-Titrate chloride solution against silver nitrate until arrive to equivalent point(the point in which the number of moles of $AgNO_3$ equal to the number of moles of chloride ion)[Notice a white precipitate in the yellow solution].

After this point the excess of $AgNO_3$ will react with potassium chromate leading to formation of red precipitate Ag_2CrO_4 (the end point).The difference between equivalent and end point is the volume of $AgNO_3$ reacted with the indicator.

4- Repeat the titration and calculate the average and subtract the indicator blank(equal to 0.1mL).Calculate the normality.

$$N_{Cl^-}\times V_{Cl^-}=N_{Ag^+}\times V_{Ag^+}$$

Concentration of $[Cl^-]_{(ppm)}$ = N_{Cl^-} × eq.wt ×1000

Experiment (7)

Oxidation-reduction reactions

Oxidation-reduction reactions: are all the reactions involving change in oxidation number or transfer of electrons among the reacting substances.

∗ **Reduction agent**: is one that loses electrons and is oxidized to a higher valiancy conditions.

Ex: Ferrous, stannous compounds, sodium thiosulphate and oxalate ion.

$$C_2O_4^{=} \rightarrow 2CO_2 + 2e^- \qquad \text{eq.wt}=134/2=67 \text{ g/g.eq}$$

∗ **Oxidation agent**: is one that gains electrons and is reduced to a lower valiancy conditions.

Ex: Potassium dichromate, potassium permanganate.

The permanganate ion in acid solution is a strong oxidizing agent, because the standard potential in acid solution E° has been calculated to be 1.51V.

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \qquad \text{eq.wt}=158.03/5=31.6 \text{ g/g.eq}$$

Preparation of solutions:

A: Preparation of 0.1N potassium permanganate.

∗ Weigh out about 3.2gm of $KMnO_4$ on a watch glass ,and transfer it to a 1500mL beaker and add 1L distilled water ,cover the beaker with a clock glass then heat the solution to boiling, boil gently for 1hr and allow the solution to cool to the laboratory temperature , filter the solution through a funnel containing a plug of purified glass wool, collect the filtrate in a vessel. The solution should be stored in a clean ,glass stoppered bottle of a dark-brown-colored glass and kept in the dark.

B: Preparation of 0.1N sodium oxalate ($Na_2C_2O_4$).

∗ Weigh out about 1.675gm of $Na_2C_2O_4$ and dissolved it in distilled water in a 250mL volumetric flask.

$$N=\frac{Wt}{eq.wt} * \frac{1000}{V(mL)}$$

$$0.1=\frac{Wt}{67} * \frac{1000}{250} \Longrightarrow Wt=1.675 \text{ gm}$$

Standardization of permanganate solution with oxalate ion:

1-Pipet 10mL of 0.1N of sodium oxalate ($Na_2C_2O_4$) in a 250mL conical flask .

2-Add by a graduated cylinder 5mL of H_2SO_4 [1:8].

3-Add some drops of potassium permanganate and heat to 55-60ºC and complete the titration by adding permanganate solution until a faint pink color persists for 30sec.
4-Calculate the normality of permanganate ion.

$$\mathbf{N_1 \times V_1 = N_2 \times V_2}$$

$$\mathbf{KMnO_4 \quad KMnO_4 \quad Na_2C_2O_4 \quad Na_2C_2O_4}$$

$$\mathbf{(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O) \times 2}$$
$$\mathbf{\underline{(C_2O_4^{=} \rightarrow 2CO_2 + 2e^- \qquad) \times 5}}$$

$$\mathbf{2MnO_4^- + 16H^+ + 5C_2O_4^{=} \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O}$$

Determination the concentration of ferrous ion:

1-Pipet 10mL of ferrous ion solution in a 250mL conical flask.
2-Add 5mL of sulphuric acid H_2SO_4[1:8].
3-Titrate the solution with standard (0.1N) $KMnO_4$ until the pink color persists.
4-Repeat the titration and then calculate the normality of ferrous ion.

$$\mathbf{V_{KMnO4} \times N_{KMnO4} = \frac{\frac{Wt\ Fe^{2+}}{55.85}}{1000}}$$

$$\mathbf{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O}$$
$$\mathbf{\underline{(Fe^{2+} \rightarrow Fe^{3+} + e^-) \times 5}}$$
$$\mathbf{MnO_4- + 8H^+ + 5\ Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}}$$

……………………………………………………………………………………..

Experiment (8)

Complexometric titration

This kind of titration is called complexometric because it involved formation of complex especially by using the compound EDTA (Ethylene Diamine Tetra Acetic acid) which forms a stable complex with metal ions especially with calcium and magnesium ions. In addition the users indicator with EDTA have also capable to form a complex with the same ions (Mg^{2+} and Ca^{2+}) but less stable than the complex formed between the metal ions and EDTA.

The total hardness of water is generally due to dissolved calcium and magnesium salts Water hardness was defined in terms of the capacity of cations in the water to replace the sodium and potassium ions in soaps and form sparingly soluble products.
There are two types of water hardness, temporary and permanent.

Temporary hardness is due to the bicarbonate ion,HCO_3^-,(sodium and magnesium bicarbonate)being present in the water. This type of hardness can be removed by boiling the water to expel the CO_2 **.**

Permanent hardness is due to the presence of the ions Ca^{2+},Mg^{2+} and $SO_4^{=}$ .This type of hardness cannot be eliminated by boiling.

Hardness is now expressed in terms of the concentration of calcium carbonate that is equivalent to the total concentration of all the multivalent cations in the sample. The determination of hardness is a useful analytical test that provides a measure of water quality for household and industries uses.

Determination of total hardness (permanent and temporary) of water

A: Determination of total hardness of water.

1-Prepare 250mL of 0.02N of EDTA solution.
2-Clean the burette and rinse with EDTA solution.
3-Pipet 10mL of hardness water and add 2mL of ammonia buffer solution (PH=10)[prepared from ammonium chloride +conc. ammonia].
4-Add 3-4 drops of Eriochrome black-T indicator and titrate with standard EDTA solution until the color changes from wine red to pure blue color.
5-Repeat the titration a few times and calculate the total hardness ($V\square_A$) of the sample of water ($Mg^{2+} + Ca^{2+}$).

Calculations

V_{EDTA}≡ Volume of EDTA which equivalent to ($Mg^{2+} + Ca^{2+}$)⇛ $V\square_A$

$$\begin{array}{cccc} N_1 \times & V_1 = & N_2 \times & V_2 \\ \downarrow & \downarrow & \downarrow & \downarrow \\ \textbf{EDTA} & \textbf{EDTA} & \textbf{Sample(?)} & \textbf{Sample} \\ \textbf{(0.02N)} & & & \end{array}$$

Total hardness (ppm)=N × eq.wt × 1000
(Concentration of $Mg^{2+} + Ca^{2+}$) $CaCO_3$

Or **Total hardness (ppm)=($V_{EDTA}/V_{solution}$)× 2000**
(Concentration of $Mg^{2+} + Ca^{2+}$)

B: Determination of the permanent hardness

1-Pipet 10mL of the hardness water and add 2mL of sodium hydroxide solution 4N (PH=12) which is sufficiently high to precipitate the magnesium quantitatively as the hydroxide.
2-Add some crystals of Murexide indicator.
3-Stirr the solution and titrate it with standard EDTA solution until the color changes from pink to a purple.
4-Repeat the titration a few times and calculate the ($V\square_B$), which is the volume of EDTA equivalent to Ca^{2+} only.

Calculations

V_{EDTA} =Volume of EDTA which equivalent to Ca^{2+} only⇛ $V\square_B$

$$N_1 \times V_1 = N_2 \times V_2$$

↓ ↓ ↓ ↓

EDTA EDTA Sample(?) Sample

(0.02N)

Permanent hardness (ppm)=N × eq.wt × 1000

(Concentration of Ca^{2+}) $CaCO_3$

Or Permanent hardness (ppm)=($V_{EDTA}/V_{solution}$)× 2000

(Concentration of Ca^{2+})

C: Determination of temporary hardness

Calculate the temporary hardness of water by subtracting the permanent hardness from the total hardness.

Temporary hardness =Total hardness – Permanent hardness = $V\square_A$ - $V\square_B$

(Mg^{2+}) (Mg^{2+} + Ca^{2+}) (Ca^{2+})

$N_1 \times (V\square_A - V\square_{B)} = N_2 \times V_2$

↓ ↓ ↓ ↓

EDTA EDTA Sample(?) Sample

(0.02N)

Temporary hardness (ppm)=N × eq.wt × 1000

(Concentration of Mg^{2+}) $CaCO_3$

<u>Or</u> Temporary hardness (ppm)=($V_{EDTA}/V_{solution}$)× 2000

(Concentration of Mg^{2+})

University of Baghdad
College of Science
Department of Chemistry

ANALYTICAL CHEMISTRY LABORATORY

Analytical Chemistry Sheet
For The First Class

Quantitative Analysis

Volumetric Analysis

The second season
2020-2021