Analytical ChemistryLab. -1-

for First Stage of Chemistry

semester 2nd

Laboratory Manual of Semimicro Qualitative & Quantitative Analysis

Prof. Dr. Abdul Ridha Al-Salihy & Dr. Wafaa AL-Qaysi

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Spatula	Glass Rod			Burette
		9	dropper	
		crucible		+



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 ببطىء 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 و عاء 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 والمحاد ا

- ينبغي على الطالب عدم لبس الحلي الذهبيه و الفضية وغير هما 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:



Quantitative analysis

The term **Quantitative analysis** involves the method by which the constituents of materials are identified. Three different methods of operation used in Quantitative analysis depending upon the amount of sample used. Macro on Quantitative 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 H₂S.

Group III (Al³⁺, Cr³⁺, Fe³⁺, Zn²⁺, Ni²⁺, Co²⁺, Mn²⁺) 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 H₂S.

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⁺, NH₄⁺) 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 ₂ C ₂ O ₄	White
* Ag ₂ CrO ₄	Red
Ag ₂ CO ₃	Yellow
AgOH	Brownish black
AgCl	White
AgCN	White
AgCNS	White
AgBr	Pal yellow
↓ AgI	Yellow
Ag ₂ S	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.

$$Ag^{+} + Cl^{-} = AgCl_{White ppt.}$$

- a) AgCl chemical decomposition when exposed to ultraviolet or to a strong sun light (distinction from PbCl₂ and Hg₂Cl₂). 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 $Ag(NH_3)_2^+$

 $Ag Cl + 2NH_4OH = Ag(NH_4)_2^+ + Cl^-$

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

$$\operatorname{Ag}(\operatorname{NH}_3)_2^+ + \operatorname{Cl}^- + 2 \operatorname{H}_3\operatorname{O}^+ = \operatorname{AgCl}_{\operatorname{White ppt.}} + 2\operatorname{NH}_4^+ + 2\operatorname{H}_2\operatorname{O}$$

 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, AgC₉H₆NO, is formed, in the present of ammonium acetate.

 $Ag^+ + C_9H_6NOH + H_2O = AgC_9H_6NO\downarrow + H_3O^+$ Yellow ppt.

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

$$Ag^+ + I^- \longrightarrow AgI \downarrow$$

Yellow p

AgI is soluble in both solutions of potassium cyanide.

$$AgI + 2CN^{-} = Ag(CN)_{2^{-}} + I^{-}$$

And sodium thiosulfate

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

4. Chromate ion solution(use K₂CrO₄solution)

Silver ion and chromate ion combine to form a red precipitate of silver chromate, Ag₂CrO₄, which is insoluble in dilute acetic acid but soluble in nitric acid and in aqueous ammonia.

 $2Ag^+ + CrO_4^= \longrightarrow Ag_2CrO_4$ Red ppt.

Identification of the Lead ion Pb²⁺

A list of some of the insoluble lead compounds is given in table 2 below: Table 2 Insoluble lead compounds with their colors

	1
Compound	color
PbCl ₂	White
* PbBr ₂	White
PbF ₂	White
PbI ₂	Orang-yellow
PbSO ₄	White
Pb(OH) ₂	White
PbC ₂ O ₄	White
PbCO ₃	White
↓ PbCrO ₄	Yellow

Pb3(PO4)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, PbCl₂ is formed.

 $Pb^{++} + 2Cl^{-} \longrightarrow PbCl_2$ White ppt.

- a) PbCl₂ chemical decomposition is **not affected** by ultraviolet or to a strong sun light (distinction from AgCl and Hg₂Cl₂).
- b) PbCl₂ is soluble in hot water, but separates again, as white upon cooling the solution.
- Sulfate ion solution (use dilute H₂SO₄). Lead ion and sulfate ion combine to form a white precipitate of lead sulfate (PbSO₄)

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

PbSO₄ is soluble in concentrated solution of ammonium acetate.

 $PbSO_4 + 2C_2H_3O_2 = Pb (C_2H_3O_2)_2 + SO_4^{2-1}$ In solution

 3. Chromate ion solution(use K₂CrO₄solution) Lead ion and chromate ion combine to form a yellow precipitate of lead chromate, PbCrO₄.
 Pb⁺⁺ + Cr O₄⁼ — PbCrO₄ Yellow ppt.

PbCrO₄, which is soluble in nitric acid and in alkali hydroxides.

 $\begin{array}{c} PbCrO_{4} + H_{3}O^{+} = & Pb^{++} + HCrO_{4}^{-} + H_{2}O \\ PbCrO_{4} + 4OH^{-} = & PbO_{2}^{2^{-}} + CrO_{4}^{2^{-}} + 2H_{2}O \end{array}$

4. Sulfide ion solution (use H₂S which means Thioacetamide CH₃CSNH₂) Lead ion and sulfide ion combine to form a black precipitate of lead sulfide, PbS.

Pb⁺⁺ + H₂S + 2H₂O \longrightarrow PbS \downarrow +2 H₃O⁺ Black ppt. PbS, which is soluble in hot dilute nitric acid. $3PbS + 8 H_3O^+ + 2NO_3^- = 3Pb^{2+} + 2NO + 12 H_2O + 3S^-$

B. Identification of the Mercurous ion Hg₂²⁺

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 ₂ Cl ₂	White
Hg2C2O4	White
Hg ₂ Br ₂	Whitish yellow
Hg ₂ CO ₃	Yellowish brown
Hg ₂ I ₄	Yellow
\bullet Hg ₂ S	black

* Decreasing Concentration of Hg_2^{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, Hg₂Cl₂ is formed.

$$Hg_2^{2+} + 2Cl^- \longrightarrow Hg_2Cl_2$$

White ppt

- a) When Hg₂Cl₂ exposed to ultraviolet or to a strong sun light a bright reddish orange fluorescence is noticed (distinction from PbCl₂ and AgCl).
- b) Hg₂Cl₂ turns to a black mixture when treated with aqueous ammonia.

$$Hg_{2}Cl_{2} + 2NH_{3} = HgNH_{2}Cl + Hg + NH_{4} + Cl^{-1}$$

White ppt. HgNH_{2}Cl + Hg + NH_{4} + Cl^{-1}

This mixture of HgNH₂Cl and Hg is soluble in concentrated nitric acid. $2HgNH_2Cl + 4H_3O^++2NO_3^- \longrightarrow 2Hg^{2+}+N_2+2NO+8$ H₂O +2Cl⁻ $3Hg + 8H_3O^++2NO_3^- \longrightarrow 3Hg^{2+}+2NO+12$ H₂O

2. Aqueouse Ammonia

Mercurous ions form when react with aqueouse ammonia a black precipitate of finely divided mercury

9

 $2Hg_{2}{}^{++} + 4NH_{3 aq.} + H_2O = Hg_2ONH_2{}^{+} + 2Hg_{Black} + 3NH_4{}^{+}$

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.

 $Hg_2^{++} + 2C_9H_6NOH + 2H_2O \longrightarrow Hg_2(C_9H_6NO)_2 + H_3O^+$ Yellow ppt.

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 (SnCl₄ solution)

Stannous chloride reduces the mercuric ion to the mercurous ion giving a white precipitate of Hg₂Cl₂.

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

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

 $Hg_2Cl_2 + SnCl_4^= = 2Hg_{Black ppt.} + SnCl_6^=$

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 Hg₂⁺⁺ can be separated from the rest of the cations by the addition of chloride ions.

Ag
$$^{+}$$
 + Cl⁻ \longrightarrow AgCl \downarrow
White ppt.
Pb²⁺ + 2Cl⁻ \longrightarrow PbCl₂ \downarrow
White ppt.
Hg₂²⁺ + 2Cl⁻ \longrightarrow Hg₂Cl₂ \downarrow
White ppt.

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 HgNH₂Cl and Hg. This black residue serves as a good indication for the presence of Hg_2^{++} .





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

Precipitation of the group			
Place 10 drops of the given solution in a test tube and add 3 drops of 3M HCl			
Heat the mixture in a water b	bath a few minutes, cool under	the tap and allow the ppt. to	
settle. test for complete ppt.	centrifuge and save the centri	fuge, wash the ppt. with 10	
drops of cold water containing	g a few drops of 3M HCl (2).		
Precipitate:		Centrifugate	
White ppt. which may	be AgCl, Hg ₂ Cl ₂ and PbCl ₂	Dist. water	
wash twice with 7 drops p	ortion of boiling water and		
combine washings (3).	-		
Centrifugate:	Residue :		
May contain Pb ⁺⁺ and	May contain AgCl and I	Hg ₂ Cl ₂ . Apply the U.V. light	
Cl ⁻ ions. Divide, while still	test on a small part of the ppt. (4). Blackening confirms Ag^+		
hot, into two parts:	ion, but reddish orange fluorescence confirms Hg_2^{++} ion. If		
Small part:	the silver ion is present the id	entification of Hg ₂ ⁺⁺ ion. May	
Add a few drops of 1M	not be clear. In this case, trea	t the white ppt. with 10 drops	
K ₂ CrO ₄ solution, yellow ppt.	of 3M warm aqueous ammonia, then centrifuge.		
of PbCrO ₄ confirms	Centrifugate	Residue:	
presence of Pb ⁺⁺ ion.	May contain Ag(NH ₃) ₂ ⁺	If black, due to	
Large pare:	and Cl ⁻ ions which give in	(Hg+HgNH ₂ Cl).Hg ₂ ⁺⁺ ion is	
Evaporate to half its	nitric acid a white ppt. of	confirmed.	
volume cool to room	AgCl indicating the		
temperature. formation of	presence of Ag ⁺ ion.		
white crystalline ppt. not			
affected by U.V. light			
confirms Pb ⁺⁺ .			

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 PbCl₂ through the formation of complex ion.

 $\begin{array}{cccc} AgCl + Cl^{-} & & AgCl_{2}^{-} \\ AgCl + 2Cl^{-} & & AgCl_{2}^{=} \\ PbCl_{2} + 2Cl^{-} & & PbCl_{4}^{=} \end{array}$

- 2. if the wash water contains no HCl, an appreciable amount of PbCl₂ 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 gro	oup I cations		
N N	Name: Unknown No.:				
Se D	ection: ate:				
N	lotes and Equat	tions :			
	Ions of	Ions found, by	Ions present in	grade	
	group I	the student	the unknown		
			solution		
	Ag ⁺				



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.

 $CH_3CSNH_2 + H_2O \longrightarrow CH_3CONH_2 + H_2S$

H₂S can also be generated by gentle heating of a mixture called, Aitch-Tu-Ess which is composed of sulfur, paraffin and asbestos.

C. 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 H₂S or 1M CH₃CSNH₂ sol)

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

 $Hg^{++} + H_2S^* + 2H_2O \longrightarrow HgS + 2H_3O^+$ Black ppt.

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).

$$3HgS + 2NO_3^- + 8H_3O^+ + 12Cl^- \longrightarrow 3HgCl_4^= + 2NO + 3S + 12H_2O$$

* 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 Hg₂Cl₂.

 $SnCl_4^{=} + 2HgCl_2 \longrightarrow SnCl_6^{=} + Hg_2Cl_2$ White ppt.

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

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

 $SnCl_4^{=} + Hg_2Cl_2 \longrightarrow Hg + SnCl_6^{=}$ Black ppt.

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, HgI₂

 $Hg^{++} + 2I^{-} \longrightarrow HgI_2$ Red ppt.

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

 $HgI_2 + 2I^- \longrightarrow HgI_4^-$

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 $0.1M \text{ Co}(NO_3)_2$ solution and stirring thoroughly with dropwise addition of 0.1M ammonium thiocyanate solution.

 $Hg^{++} + Co^{++} + 4CNS^{-} \longrightarrow HgCo(CNS)_{4}$ Deep blue ppt.

D. 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

|--|

	BiOCl	White
*	BiI ₃	Reddish or brownish-gray
	BiAsO ₄	White
	(BiO)OH	White
	BiPO ₄	White
	Bi(OH) ₃	White
	Bi ₂ S ₃	Brown

* Decreasing Concentration of Bi⁺⁺⁺ Ion

1. Sulfide ion solution (use H₂S or CH₃CSNH₂)

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

 $2Bi^{+++} + 3H_2S + 6H_2O \longrightarrow Bi_2S_3 + 6H_3O^+$ Brown-black ppt.

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

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

2. Aqueous ammonia

Bismuth forms a white precipitate of bismuth hydroxide, Bi(OH)₃, when reacts with aqueous ammonia.

 $Bi^{+++} + 3NH_3 aq. + 3 H_2O \longrightarrow Bi(OH)_3 + 3NH_4^+$ White ppt.

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, Na₂SnO₂, 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.

 $Sn^{++} + 2OH^{-} = Sn(OH)_{2}$ $Sn(OH)_{2} + 2OH^{-} = SnO_{2}^{=} + 2H_{2}O$ $2Bi^{+++} + 3SnO_{2}^{=} + 6OH^{-} = 2Bi + 3SnO_{3}^{=} + 3H_{2}O$ or $2Bi(OH)_{3} + 3SnO_{2}^{=} = 2Bi + 3SnO_{3}^{=} + 3H_{2}O$ Black ppt.

E. <u>Identification of the Cupric ion Cu⁺⁺</u>

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 H₂S or CH₃CSNH₂)

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

 $Cu^{++}+ 3H_2S + 2H_2O = CuS + 2H_3O^+$ Black ppt.

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

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

2. Aqueous ammonia

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

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

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

 $Cu(NH_3)_{4^{++}} + 4H_3O^+ \longrightarrow Cu^{++} + 4NH_4^+ + 4H_2O$

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

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.

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

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

4. Potassium ferrocyanide solution (use K₄[Fe(CN)₆] solution).

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

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

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.

 $2Cu^{++} + 4I^{-} \underbrace{\qquad Cu_{2}I_{2}}_{(\text{yellowish- brown ppt.})} + I_{2}$ $I_{2} + I^{-} \underbrace{\qquad I_{3}}_{-}$

F. 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 ₂ O 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 H₂S or CH₃CSNH₂)

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.

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

Yellow ppt.

2. Aqueous ammonia

A white precipitate of cadmium hydroxide, Cd(OH)₂, is formed when cadmium ion reacts with aqueous ammonia.

 $Cd^{++} + 2NH_{3 aq.} + 2H_2O \xrightarrow{} Cd(OH)_2 + 2NH_4^+$ White ppt.

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

 $Cd(OH)_2 + 4NH_3 aq. - Cd(NH_3)_4^{++} + 2OH^{-1}$

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

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.

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

Sulfide from group II (insoluble in 0.3M		Sulfide from g	roup III (soluble in 0.3M
	HCl)		HCl)
Sulfide	<u>Ks.p.</u>	Sulfide	<u>Ks.p.</u>
PbS	3.4 x 10 ⁻	MnS	1.4 x 10 ⁻
28		15	
CdS	3.6 x 10 ⁻	FeS	3.7 x 10 ⁻
29	0.7.10		5 0 10
CuS	8.5×10^{-1}	CoS	7.0×10^{-1}
Has	2 0 x 10-		2 0 v 10-
53 ПВ	5.0 X 10	23	5.0 X 10
Bi2S2	1.6 x 10 ⁻	NiS	1 4x 10 ⁻
72 DI203	1.0 x 10	24	1.44.10
Sb ₂ S ₃	1.6 x 10 ⁻		
93			

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

The Copper group Analysis of group II cations





Procedure NO. 2 Separation and identification of Group II cations

Precipitation of the group		
Place 10 drops of the given solution	on in a test t	ube and adjust the acidity to 0.3M HCl
(1) by using 1M HCl. Add 10 drops of H_2S a	nd then heat	to boiling for a few minutes, centrifuge
and test the solution for complete precipitat	ion of the gr	oup cations as sulfides by heating and
passing H ₂ S again stirr well and centrifuge.		
Precipitate:		Centrifugate
Add 10 drops of 3M HNO ₃ upon the p	ot. with stir,	Groups III-V cations
and heat in water bath for 3 minutes and cent	rifuge .	
Precipitate:	Centrifugate	2
May contain HgS (b) or	Contains	Pb ⁺⁺ , Bi ⁺⁺⁺ , Cu ⁺⁺ and Cd ⁺⁺ ions. Make
Hg(NO ₃) ₂ .2HgS (w), dissolve in 5 drops of	the sol.	basic by dropwise addition of
aqua regia, add 10 drops of water, then heat	concentrate	d aq. Ammonia with stirring until
for about 3 minutes (under hood). Cool	about 3 dro	ops in excess of conc. NH ₃ has been
then add 2 drops of $SnCl_2$ sol. white ppt.,	added (test]	litmus). Then centrifuge.
Hg_2Cl_2 or gray (Hg + Hg_2Cl_2) confirms		
presence of Hg ⁺⁺ ion.		

Description		Control Constant
Precipitate :		Centriugate :
This ppt. contain	ns the hydroxides of Pb ⁺⁺	May be contains $Cu(NH_3)_4^{++}$ and
and Bi ⁺⁺⁺ as Pb(OH) ₂ ,	Bi(OH) ₃ , add 4 drops of	Cd(NH ₃) ₄ ⁺⁺ complex ions, if solution is
NaOH and place in the	boiling water for 2 min.	deep blue Cu^{++} ion is confirmed (4). (If
and centrifuge.		necessary concentrate the solution to 1 ml
		by gentle heating), divide the solution into
		two parts:
		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.
Centrfriugate:	Precipitate :	Second portion:
This solution	This white ppt.	Acidify with diluted acetic acid and
contains Na ₂ [PbO ₂]	contains bismuth	add 1 drop of potassium ferrocyanide
which acidify with	hydroxide Bi(OH) ₃ ,	solution, $K_4[Fe(CN)_6]$. The formation of
diluted acetic acid and	wash with 10 drops of	reddish-brown precipitate means the Cu ⁺⁺
then add 2 drops of	water and prepare	ions is found.
potassium chromate sodium stannite (2), (3)		
K_2CrO_4 a yellow ppt.	to sol. from which 10	
of PbCrO ₄ will	drops of are poured upon	
appears.	the ppt. immediate	
	blackening of the ppt.	
	(Bi) confirms Bi ⁺⁺⁺ ion.	

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 ₃ O ⁺
Blue-green	$0.3 \text{ M H}_{3}\text{O}^{+}$
Yellow-green	0.5 M H ₃ O ⁺
Yellow	$1.0 \text{ M H}_3\text{O}^+$ and higher

1 drop		1 drop
HCl	21	NH4OH

Blue	Green (Q.3M)	←	Yellow
If the color of solution is blue,			If the color of solution is yellow,
The solution will be alkaline			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, Na₂SnO₃, 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 :	

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 $Al_2O_3.xH_2O$

or, $Al^{+++} + 3NH_3$ aq. $+ 3H_2O = Al_2O_3.xH_2O_White ppt.$ $Al^{+++} + 3NH_3$ aq. $+ 3H_2O = Al(OH)_3 + 3NH_4^+$

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.

$$Al^{+++} + 3OH^{-} \longrightarrow Al(OH)_{3}$$

$$Al(OH)_{3} + OH^{-} \longrightarrow Al(OH)_{4}^{-}$$
or,
$$Al(OH)_{3} + OH^{-} \longrightarrow AlO_{2}^{-} + 2H_{2}O$$

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 .

 $Al^{+++} + 3C_9H_6NOH + 3H_2O = Al(C_9H_6NO)_3 + 3H_3O^+$ Yellow-green ppt.

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
\sim Cr(OH) ₃	Yellowish-green
CrAsO ₄	Light green
CrPO ₄	Green With (4H ₂ O)
•	or violate (3 OR 6H ₂ O)

* 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 $Cr_2O_3.xH_2O$ $Cr^{+++} + 3 NH_3 aq. + 3H_2O \longrightarrow Cr(OH)_3 + 3NH_4^+$ Grayish-green ppt.

 $Cr(OH)_3$ is readily dissolves in acids, but slightly soluble in excess aqueous NH₃ in the cold giving a violate or pink solution of the chromic complex ion, $Cr(NH_3)_6^{+++}$ $Cr(OH)_3 + 6$ NH₃ aq. \longrightarrow $Cr(NH_3)_6^{3+} + 3OH^-$

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.

or, $Cr^{+++} + 3 OH^{-} \longrightarrow Cr(OH)_{3}$ $Cr(OH)_{3} + OH^{-} \longrightarrow Cr(OH)_{4}^{-}$ $Cr(OH)_{3} + OH^{-} \longrightarrow CrO_{2}^{-} + 2H_{2}O$ Green

2. Sodium peroxide Na₂O₂,(or using H₂O₂ and NaOH sol.)

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

 $\begin{array}{c} Cr^{+++} + 3 \text{ OH}^{-} = & Cr(OH)_{3} \\ Cr(OH)_{3} + OH^{-} = & Cr(OH)_{4}^{-} \\ 2Cr(OH)_{4}^{-} + 3 \text{ O}_{2}^{=} = & CrO_{4}^{2-} + 4OH^{-} + 2H_{2}O \end{array}$

The chromate ion is precipitated as a yellow PbCrO₄ or BiCrO₄

 $CrO_4^{=} + Ba^{++} = BaCrO_4$ $CrO_4^{=} + Pb^{++} = PbCrO_4$ YellowYellow

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 .

 $HCrO_{4} + 2 H_2O_2 + H_3O^+ - CrO_5 + 4H_2O$

 CrO_5 is unstable in aqueous solution, and readily with the liberation of oxygen. 4 $CrO_5 + 12 H_3O^+ = 4 Cr^{+++} + 7O_2 + 18H_2O$

The test for chromium ion may be done as follows:

Precipitate the $CrO_4^{=}$ ion as PbCrO₄. dissolve the precipitate in hot 3M HNO₃, cool to room temperature and add equal volume of amyl alcohol followed by about 1 ml 3% H₂O₂. 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
*	$Fe_{2}(SeO_{3})_{3}$ $Fe_{4}[Fe(CN)_{6}]_{3}$ $Fe(OH)_{3}$ $FePO_{4}$ $Fe_{2}S_{3}$	Deep blue Reddish brown Yellowish white black

* Decreasing Concentration of Fe+++ Ion

1. Hydroxide ion solution (NH₃ 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.

 $Fe^{+++} + 3 NH_3 aq. + 3H_2O = Fe(OH)_3 + 3NH_4^+$ (Reddish-brown) ppt.

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 $Cr_2O_3.xH_2O$.

 $2 \text{ Fe}^{+++} + 6 \text{ OH}^{-} + (x-3) \text{ H}_2\text{O} = \text{Fe}_2\text{O}_3.x\text{H}_2\text{O}$

2. Sulfide ion solution $(H_2S \text{ or } (NH_4)_2S)$

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

 $2 \operatorname{Fe}^{+++} + \operatorname{H}_2S + 2\operatorname{H}_2O = 2\operatorname{Fe}^{++} + \operatorname{S}_{\bigvee} + 2\operatorname{H}_3O^+$ Yellow

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

 $2 \operatorname{Fe}^{+++} + 3 \operatorname{S}^{=} \longrightarrow \operatorname{Fe}_2 \operatorname{S}_3$ Black ppt.

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

 $Fe_2S_3 + 4 H_3O^+ = 2Fe^{++} + 2H_2S + 4H_2O + S$

3. Thiocyanate ion, CNS⁻, solution (use NH₄CNS 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⁺⁺.

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

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.

 $Fe^{+++} + 3 C_9H_6NOH + 3H_2O \longrightarrow Fe(C_9H_6NO)_3 + 3H_3O^+$ Dark green ppt.

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

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 ₂ O 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

 $Fe^{++} + 2 NH_3 + 2 H_2O = Fe(OH)_2 + 2NH_4^+$ White

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 = Fe(OH)_3 (Reddish-brown)

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.

 $Fe^{++} + 2OH^{-} = Fe(OH)_2$ White

2. Sulfide ion solution (H₂S or (NH₄)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.

 $Fe^{++} + H_2S + 2 H_2O = FeS + 2 H_3O^+$ The precipitate is soluble in acids giving off hydrogen sulfide.

3. Ferrocyanide ion, $Fe(CN)_6^{3-}$ solution (use K₄Fe(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, K₂[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].

 $Fe^{++} + 4 K^{+} + Fe(CN)_{6}^{3-} = K_{2}[Fe(Fe(CN)_{6}] + 2K^{+}]$ White

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

 $Fe^{++} + 3 K^+ + Fe(CN)_6^{3-} \longrightarrow KFe(Fe(CN)_6 + 2K^+)_{Deep blue}$

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

 $2 Fe^{++} + 3 S^{=} = Fe_2S_3$

Black ppt.

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 ₂ O 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)NO₃ is formed when aqueous ammonia is added to a solution of cobaltous nitrate.

$$Co^{++} + NO_3^- + NH_3 aq. + H_2O = Co(OH)NO_3 + NH_4^+$$

Black

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

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

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.

$$Co^{++} + 2 OH^{-} = Co(OH)_2 \downarrow$$

Pink

 $Co(OH)_2 + 2 OH^- - CoO_2^- + 2H_2O$

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.

 $2 \operatorname{Co}(OH)_2 + O_2 + 2 \operatorname{H}_2O = 2 \operatorname{Co}(OH)_3 + 2OH^{-1}$ Brown

3. Sulfide ion solution (H₂S or (NH₄)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.

$$Co^{++} + H_2S + 2 H_2O = CoS + 2 H_3O^+$$

Black ppt.

Cobaltose sulfide in insoluble in a very dilute acids and in acetic acid, but dissolved readily by concentration HCl, HNO₃ and by aqua regia. In the case of HCl, CoS dissolves quite slowly.

$$\begin{array}{c} CoS + 2 H_3O^+ = & Co^{++} + H_2S + 2 H_2O \\ CoS + 4 H_3O^+ + 2 NO_3^- = & Co^{++} + 2 NO_2 + S + 6 H_2O \end{array}$$

4. Thiocyanate ion

when an alcoholic solution of NH₄CNS 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.

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

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 NH₄CNS 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:

Compound		color	
	Ni(IO ₃) ₂	Yellow	
*	NiCO ₃	Light green	
	Ni(OH) ₂	Green	
	Ni(CN) ₂	Green	
	NiS	Black	

 Table 14 Insoluble nickelous compounds with their colors

* 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.

 $Ni^{++} + 2 OH^{-} = Ni(OH)_2$ 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 $Ni(NH_3)_6^{++}$

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

 $Ni(NH_3)_{6^{++}}$ 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.

 $Ni^{++} + Cl^{-} + NH_3 aq. + H_2O \longrightarrow NiOHCl + NH_4^+$ Green ppt.

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

NiOHCl + 7 NH₃ aq. + H₂O \longrightarrow Ni(NH₃)₆⁺⁺ + NH₄⁺ + Cl⁻ + 2 OH-Violate-blue

3. Sulfide ion solution $(H_2S \text{ or } (NH_4)_2S)$

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

 $Ni^{++} + H_2S + 2 H_2O = NiS + 2H_3O^+$

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:-

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

4. Dimethylglglyoxime, C₄H₈O₂N₂ 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.

 $Ni^{++} + 2 C_4H_8O_2N_2 + 2 NH_3 aq. = Ni(C_4H_7O_2N_2)_2 + 2 NH_4^+ Red ppt.$

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.

 $Mn^{++} + 2 NH_3 + 2 H_2O = Mn(OH)_2 + 2NH_4^+$ White

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, $Mn(OH)_2$

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

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 .xH₂O.

 $4 \operatorname{Mn}(OH)_2 + O_2 + 2 \operatorname{H}_2O = 4 \operatorname{Mn}(OH)_3$ Brown ppt.[

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

 $Mn^{++} + 2 OH^{-} \longrightarrow Mn(OH)_{2}$ $4 Mn(OH)_{2} + O_{2}^{=} + H_{2}O \longrightarrow MnO(OH)_{2} + 2OH^{-}$ or, $Mn(OH)_{2} + O_{2}^{=} + xH_{2}O \longrightarrow MnO_{2}.xH_{2}O + 2OH^{-}$ Brown
Brown

3. Sulfide ion solution (H₂S or (NH₄)₂S sol.)

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

 $Mn^{++} + H_2S + 2 NH_3 aq. \longrightarrow MnS + 2 NH_4^+$

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 NaBiO₃).

Manganous ions, in a cold solution containing dilute nitric acid are oxidized by the bismuthate ions (usually added as solid NaBiO₃) to the reddish purple or violet-red permanganate ions NnO_4^- .

 $2 \text{ Mn}^{++} + 5 \text{ BiO}_3^- + 14 \text{ H}_3\text{O}^- = 2\text{MnO}_4^- + 5\text{Bi}^{+++} + 21\text{H}_2\text{O}$

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 PbO₂, (NH₄)S₂O₈ and KIO₄ 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	
T	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.

 $Zn^{++} + 2 NH_3 aq. + 2 H_2O = Zn(OH)_2 + 2 NH_4^+$ $Zn(OH)_2 + 4 NH_3 aq. = Zn(NH_3)_4^{++} + 2 OH^-$

b. Alkali hydroxide solutions .

Zinc ion reacts with the alkali solution giving a white gelatinous precipitate of zinc hydroxide, Zn(OH)₂

 $Zn^{++} + 2 OH^{-} = Zn(OH)_2$ White

 $Zn(OH)_2$ is soluble in excess of the precipitant, $Zn(OH)_2 + OH^- = Zn(OH)_3^-$

or, $Zn(OH)_2 + 2 OH^- = ZnO_2^- + 2H_2O$ And also soluble in dilute acids, $Zn(OH)_2 + 2 H_3O^+ = Zn^{++} + 4 H_2O$

3. Sulfide ion solution $(H_2S \text{ or } (NH_4)_2S)$

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. $ZnS + 2 NH_4^+$ White

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 H₂S, the precipitate of ZnS will be formed.

 $\begin{array}{c} Zn(NH_3)_{4^{++}} + 4 \ HC_2H_3O_2 = & Zn^{++} + 4 \ NH_4{}^+ + 4 \ C_2H_3O_2{}^- \\ Zn^{++} + H_2S + 2 \ H_2O = & ZnS + 2H_3O^+ \\ & \text{White ppt.} \end{array}$

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

 $ZnS + 2H_3O^+ = Zn^{++} + H_2S + 2H_2O$

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 $Zn(C_9H_6NO)_2$.

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

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 HNO₃. when dissolution is complete, the group can then be divided into two subgroups, by the action of excess KOH or NaOH solution and Na₂O₂. 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

NH4Cl H₂S or CH₃CSNH₂, NH₃, C.F, heat







Procedure NO. 3 Analysis of Group III cations

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.

Precipitate:		Centrifugate
Contains FeS (b), CoS (b), NiS (b),	Contains groups IV and V Acidify	
ZnS (w), Al(OH) ₃ (w), Fe(OH) ₃ (r-br), C	r(OH) ₃ (gr-	immediately with hydrochloric acid
grn). Wash twice with water and discard was	shing. Treat	and boil (2) to 1 ml, discarding any
the ppt. with 5 drop of concentrated HCl.		ppt. which may form reserve the
Stir thoroughly for about a minute.	If the ppt.	colorless sol. for the analysis of
dissolves completely, Ni and Co must be	absent (3).	groups IV and V cations.
Add 3 drops of concentrated HNO ₃ and he	eat until the	
precipitate dissolves. Make the solution bas	tic with 3M	
KOH sol. then , slowly and carefully, add (0.2 gram of	
Na ₂ O ₂ (4), (5). Heat for a few minutes and	centrifuge.	
Wash the residue with 10 drops of water an	nd combine	
washing with centrifuge.		
Precipitate of subgroup IIIB cations	Centrifugate	e (subgroup IIIA cations)
Contains $MnO_2.xH_2O_3$, $Co(OH)_3$,	Conta	ins AlO_2^- , $ZnO_2^=$, and $CrO_4^=$ ions.
Ni(OH) ₂ and Fe(OH) ₃ . Wash with 10 drops	Treat accord	ling to procedure No.1
of water treat according to procedure No. 2		
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:

 $\begin{array}{c} Co^{++} + H_2S + 2H_2O & \longrightarrow CoS + 2H_3O^+ \\ NH_3 + H_3O^+ & \longrightarrow & NH_4^+ + H_2O \end{array}$

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 $Mg(OH)_2$ can not be precipitated.

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

$$S^{=} + 2H_3O^{+}$$
 $H_2S + 2H_2O$

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

 $S^{=} + 2O_2$ $SQ_4^{=}$

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 SrSO₄ and BaSO₄ 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 HNO₃ 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 IIIA cations

disappeared, add 3 drops of saturated

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: Centrifugate				
May contain gelatinous white ppt. May contain $Zn(NH_3)_4^{++}$ and $CrO_4^{=}$ add				
Al(OH) ₃ , wash with 10 drops water, then dropwise 1M of barium acetate $Ba(C_2H_3O_2)$				
dd 3M HCl drop by drop until the ppt. solution until precipitation is complete. The				

centrifuge.

ammonium acetate solution and divided	Precipitate,	Centrifugate,	
into two unequal parts.	$BaSO_4 \qquad (1)$	Contains Zn(NH ₃) ₄ ⁺⁺	
Large porting:	BaCrO ₄ (y), add 10	acidify with 3M	
Add 2-3 drops of aluminon solution	drops of HCl and	CH ₃ COOH and divided	
then render basic with 3M of aq.	warm for 1 min. in a	into two unequal parts:	
ammonia. Formation of red ppt. confirms	Water bath.	Large porting:	
presence of Al ⁺⁺⁺ ion.	Centrifuge and	Saturate with H ₂ S	
Smaller part:	discard the white ppt.	and warm in a water bath	
Make the solution almost neutral	(BaSO ₄). Add 10	for few minutes, a white	
with 3M aq. ammonia, then add 5 drops	drops of amyl alcohol	ppt. of ZnS confirms	
of 8-quinolinol solution. Formation of a	and 5 drops of H_2O_2 presence of Zn^{++} ion		
greenish yellow ppt. which is little soluble	and shake well. A	the ppt. is not white	
in acetone or ethanol and highly	blue upper layer	(3) or fails to form, use	
fluorescent, confirms presence of Al+++	(2) containing CrO_5 then the smaller part.		
ion.	confirms presence of	f Smaller part:	
	Cr ⁺⁺⁺ ion.	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 BaSO₄ 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 MnO₂xH₂O, 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	2 nd. Portion	3ed. Portion	4 th. Portion
Test for Fe ⁺⁺⁺	Test for Mn ⁺⁺	Test for Co ⁺⁺	Test for Ni ⁺⁺

Divided into two parts	Add 0.2 gram of	Add with stirring	Add with stirring
a and b	NaBiO ₃ and shake	enough solid NaF	enough solid NaF
Part a	well for a minute	(2) that undissolved	(2) that undissolved
Add 2 drops of	then centrifuge	amount remains	amount remains Add
Add 2 drops of	raddish numla	Carafully lat 10 drops	2M ag ammonia dron
SM INH4CINS SOI. deep	reduisii-purpie	Calefully let 10 drops	Sivi aq. animonia diop
red coloration proves	centrifugate , MnO_4^-	alcoholic NH ₄ CNS	by drop until the
presence of Fe ⁺⁺⁺ .	ion proves presence	sol(3), rundown side	solution is slightly
Part b.	of Mn ⁺⁺ ion.	of the test tube	basic. Add 4 drops of
Make solution		containing the test	dimethylglyoxime
almost neutral with		solution. Formation	sol. formation of a red
3M aqueous ammonia,		of a blue-green ring	precipitate proves
then add 3 drops of 8-		proves presence of	presence of Ni ⁺⁺ ion
quinolinol solution.		Co ⁺⁺ ion.	(4).
Deep greenish-black			
coloration, or fine			
precipitate			
(1) proves presence of			
Fe ⁺⁺⁺ ion			

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	Ions present in the	grade
	student	unknown solution	
Al ⁺⁺⁺			
Cr ⁺⁺⁺			
Fe ⁺⁺⁺			
Co ⁺⁺			
Ni ⁺⁺			
\mathbf{Mn}^{++}			
\mathbf{Zn}^{++}			

Signature of the student

Signature of the grader



<mark>Volumetric analysis</mark>

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 <u>reactant</u>. 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 <u>visual</u> 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 acidbase 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.

M= -	Weight		1000	
	M.Wt *	Volume(mL)		

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

NT	Weight		1000	
N= -	eq.wt	- *	Volume(mL)	

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

ppm=-	weight solute(mg)		
	Volume solution(L)		

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

 $ppm = M \times M.wt \times 1000$

.....

For titrimetric reaction:

 $\begin{array}{rl} a \ A \ + \ b \ B \ \rightarrow \ product \\ titrant \ titrand \\ \mbox{At equivalent point:} \\ no.mmol \ of \ titrant(A) = no.mmol \ of \ titrand(B) \\ N_A \ \times \ V_A \ = \ N_B \ \times \ V_B \\ \mbox{or} \ M_A \ \times \ V_A \ \ \times \ R = \ M_B \ \times \ V_B \end{array} (R=b/a)$

<u>Equivalent weights</u>

(1)Equivalent weight in neutralization reactions.

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

<u>Ex</u>: equivalent weight of H₂SO₄ =M.Wt H₂SO₄/2 equivalent weight of H₃PO₄ =M.Wt H₃PO₄/3

eq.wt acid =	M.Wt acid		
	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

eq.wt base= <u>M.Wt base</u> 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.

og wt -	Formula weight (gm/mole)		
eq.wi =	No. of lost or gained electrons		

eq.wt MnO₄⁻ =
$$\frac{F.wt MnO_4}{5}$$
 eq.wt C₂O₄⁻ = $\frac{F.wt C_2O_4}{2}$

(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 AgNO₃ is: **AgNO₃ + NaCl \rightarrow AgCl + NaNO₃ eq.wt (AgNO₃) = \frac{\text{F.wt AgNO}_3}{1}**

Lab.6

Experiment (1)

A: Preparation of approximately (0.1N) HCl

1-Calculate the normality of the concentrated HCl :

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

N= 1.18 *35.4/100 *1000/ 36.5

N = 11.4 eq/L

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

 $N_1 \times V_1 = N_2 \times V_2$ conc.HCl dil.HCl $11.4 \times V_1 = 500 \times 0.1$ $V_1 = 4.5 \text{ mL}$

Transfer distilled water to a glass-Stoppard bottle and add about 4.5 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.

Weight			1000	
^{IN=} equiv	alent weight	*	Volume(mL)	

.....

Experiment (2)

Standardization of HCl solution with standard solution of Na₂CO₃

- 1-Clean the burette and rinse with HCl solution.
- **2-**Fill the burette with HCl.
- **3-**Pipet 10 ml of standard solution (Na₂CO₃) 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 :

 $Na_2CO_3 + HCl \qquad \qquad M.O \\ H_2CO_3 + 2NaCl$



Experiment (3)

Analysis of sodium carbonate Na₂CO₃

1-Clean the burette and rinse with standardized HCl solution and then fill it with the acid.

2-Pipet 10 ml unknown solution (Na₂CO₃) 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.

	First titration	Second titration	Third titration	Average of
				titrations
Titration with	V1	V1	V1	V1 (av.)
ph.ph				
Titration with	V2	V2	V2	V2 (av.)
М.О				

6- Make a table as bellow:-

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

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

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

7- The equation of reaction :



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:

 $(X-Y)=Z \rightarrow Volume of HCl which equivalent to OH^{-} \dots (1)$ $2 \times Y \rightarrow Volume of HCl which equivalent to CO₃⁼ \dots (2)$ N acid × V acid = N base × V base $N acid × Z = N OH^{-} × 10 \dots (1)$ $N acid × 2Y = N CO₃⁼ × 10 \dots (2)$ $Concentration of [OH^{-}](ppm)= N OH^{-} × eq.wt × 1000$ Concentration of [CO₃⁼](ppm)= N CO₃⁼ × eq.wt × 1000 $\dots (2)$ Concentration of [CO₃⁼](ppm)= N CO₃⁼ × eq.wt × 1000 $\dots (2)$ Concentration of [CO₃⁼](ppm)= N CO₃⁼ × eq.wt × 1000 $\dots (2)$

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 CO₃⁼

Y=Volume of HCl≡1/2 CO₃⁼ + HCO₃⁻

 $(Y-X)=Z \rightarrow Volume of HCl which equivalent to HCO_3^-$ (1)

 $2 \times X \rightarrow Volume of HCl which equivalent to CO_3^=$(2)

 $\mathbf{N}_{\text{acid}} \times \mathbf{V}_{\text{acid}} = \mathbf{N}_{\text{base}} \times \mathbf{V}_{\text{base}}$

 $N_{acid} \times Z = N HCO_3^- \times 10$ (1)

 $N_{acid} \times 2X = N CO_3^{-} \times 10$ (2)

Concentration of [HCO₃⁻]_(ppm)= N HCO₃⁻ × eq.wt ×1000

Lab.8

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.

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

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.

$2AgNO_3 + K_2CrO_4 \Leftrightarrow Ag_2CrO_4 + 2KNO_3 \qquad Ksp_{Ag2CrO_4} = 1.7 \times 10^{-12}$

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 $[Cl^-]_{(ppm)} = N_{Cl} \times eq.wt \times 1000$



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.

$$C_2O_4^- \rightarrow 2CO_2 + 2e^-$$
 eq.wt=134/2=67 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.

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

Preparation of solutions:

A: Preparation of 0.1N potassium permanganate.

* Weigh out about 3.2gm of KMnO₄ 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 (Na₂C₂O₄).

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

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

$$53$$

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

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 H₂SO₄ [1:8].

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

 $\begin{array}{rcl} N_1 \times V_1 &=& N_2 \times V_2 \\ KMnO_4 & KMnO_4 & Na_2C_2O_4 & Na_2C_2O_4 \end{array}$

 $(\operatorname{MnO_4^-} + 8H^+ + 5e^- \rightarrow \operatorname{Mn^{2+}} + 4H_2O) \times 2$ $\underbrace{(C_2O_4^- \rightarrow 2CO_2 + 2e^-) \times 5}$

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

Determination the concentration of ferrous ion:

1-Pipet 10mL of ferrous ion solution in a 250mL conical flask.

2-Add 5mL of sulphuric acid H₂SO₄[1:8].

3-Titrate the solution with standard (0.1N) KMnO₄ until the pink color persists.

4-Repeat the titration and then calculate the normality of ferrous ion.

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

 $\begin{array}{c} MnO_4^- + 8H^+ + 5e^- \to Mn^{2+} + 4H_2O \\ \underline{(Fe^{2+} \to Fe^{3+} + e^-) \times 5} \\ MnO_{4^-} + 8H^+ + 5 \ Fe^{2+} \to Mn^{2+} + 4H_2O + 5Fe^{3+} \end{array}$



Experiment (8)

Complexometric titration

This kind of titration is called complexometric because it involved formation of complex especially by using the compound EDTA (<u>E</u>thylene <u>D</u>iamine <u>T</u>etra <u>A</u>cetic 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 (Mg²⁺ and Ca²⁺) 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 ($V\Box_A$) of the sample of water (Mg²⁺ + Ca²⁺).

Calculations

V_{EDTA} = Volume of EDTA which equivalent to $(Mg^{2+} + Ca^{2+}) \Rightarrow V \Box_A$

 $\begin{array}{cccc} \mathbf{N}_1\times \mathbf{V}_1 = & \mathbf{N}_2\times \mathbf{V}_2 \\ \downarrow & \downarrow & \downarrow & \downarrow \end{array}$

EDTA EDTA Sample(?) Sample (0.02N) Total hardness (ppm)=N × eq.wt × 1000 (Concentration of $Mg^{2+} + Ca^{2+}$) CaCO₃

<u>Or</u> Total hardness (ppm)= $(V_{EDTA}/V_{solution}) \times 2000$ (Concentration of Mg²⁺ + Ca²⁺)

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 Ca²⁺ only.

Calculations

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

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 = $V\Box_A - V\Box_B$ (Mg²⁺) (Mg²⁺ + Ca²⁺) (Ca²⁺)