M.Sc. CHEMISTRY LAB MANUAL

1st Semester

Prepared By
Pure & Applied Science Dept.
Chemistrty

MIDNAPORE CITY COLLEGE

M.Sc. in Chemistry

Under Choice Based Credit System (CBCS)

(Semester Programme)

SEMESTER-I

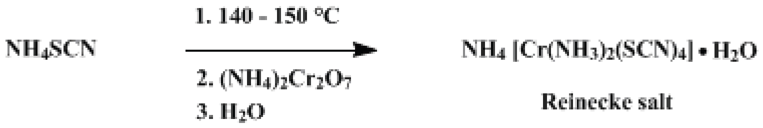
CEM 195: Inorganic Practical

Laboratory Practice Safety Rules

1. Use safety glass when dealing with fire and chemical
2. Should use apron clothes during chemistry practical
3. Always use hand wash after any type of chemical use
4. Carefully handle chemicals , glass wear, and any other instrument
5. Use dustbin always

1. Synthesis and Characterization of inorganic compounds:

1A. REINECKE SALT



$$NH_4SCN \xrightarrow[\text{2. }(NH_4)_2Cr_2O_7 \text{ 3. } H_2O]{\text{1. 140 - 150 °C}} NH_4[Cr(NH_3)_2(SCN)_4] \cdot H_2O$$

Experimental:

Chemicals:

1. Alcohol
2. Ammonia
3. Ammonium chloride
4. Ammoniumthiocyanate
5. Hydrogen cyanide
6. Acetone
7. Potassium dichromate
8. Ammonium dichromate

Apparatus:

1. Thermometer
2. Magnetic stirrer and heater
3.Suction
4.Large beaker

Synthesis of Reinecke Salt:

Procedure:

Eight hundred grams (10.5 moles) of ammonium thiocyanateis gently heated, by means of three small flames (Note 1), in a white enameled cooking pot of about 4-l. capacity. The mass is stirred with athermometer enclosed in a glass tube until the solid has partially melted and the temperature has reached 145–150°. At this point an intimate mixture of 170 g. (0.675 mole) of finely powdered ammoniumdichromate and 200 g. (2.6 moles) of ammonium thiocyanateis added in portions of 10–12 g. with constant stirring. After about ten such portions have been added a fairly vigorous reaction takes placewith evolution of ammonia and the temperature rises to 160°. The flames are extinguished, and the remainder of the mixture is added at such a rate that the heat of reaction maintains the temperature at 160° (Note 2). Stirring is continued while the mass cools, and any lumps of solid which form around thesides of the vessel are broken loose (Note 3).The product, while still warm (Note 4), is finely powdered and stirred with 750 cc. of ice water in a large beaker. After fifteen minutes the insoluble portion is filtered by suction, freed as completely aspossible from mother liquor without washing (Note 5), and stirred into 2.5 l. of water previouslywarmed to 65°. The temperature is then rapidly raised to 60° (Note 6), the solution is filtered at oncethrough a hot-water funnel, and the filtrate is placed in a refrigerator overnight.

The resulting crystals are collected and the mother liquor employed for a second similar extraction of the residue at 60°. This yields a further crop of crystalline Reinecke salt. The mother liquor is finallyconcentrated to 250–300 cc. by evaporation at 40–50° under reduced pressure, when a small third crop (12–13 g.) is obtained. The total yield of air-dried crystals is 250–275 g. (52–57 per cent of thetheoretical amount) (Note 7).The undissolved residue from the second extraction consists chiefly of Morland salt (the guanidine salt of the Reinecke acid) and amounts to 130–135 g. (33–34 per cent of the theoretical amount) (Note8).

NOTES

1. Heat must be applied as uniformly as possible.
2. The addition of the mixture requires five to seven minutes.
3. The product is detached from the walls during cooling as it is difficult to remove when

cold.

4. The material should be pulverized while warm before it has had an opportunity to attract moisture from the air.

5. The filtrate, which consists largely of unchanged ammonium thiocyanateand its decomposition products, contains too little Reinecke salt to repay further treatment.

6. Reinecke salt decomposes in aqueous solution with formation of a blue color and free hydrogen cyanide. At room temperature this decomposition occurs in about two weeks, and above 65° it takesplace quite rapidly. A similar decomposition takes place in boiling alcohol.

7. Reinecke salt is of value as a precipitant for primary and secondary amines, prolineand hydroxyproline, and certain amino acids.1

8. The Morland salt, which is soluble in acetone, contains a small proportion of a colorlesssulfur

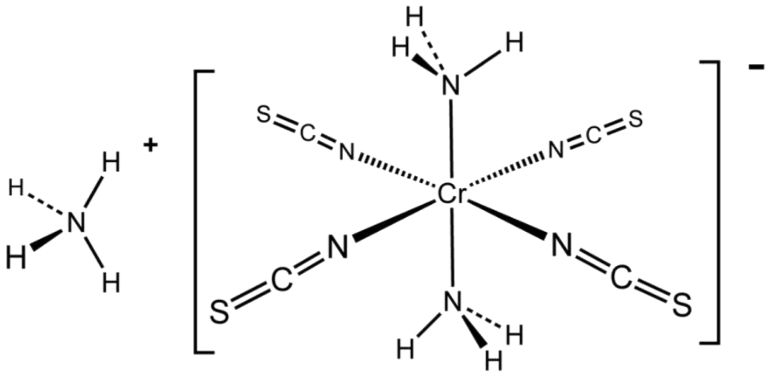
compound insoluble in hot water. It can be partially converted into Reinecke salt by treatment in dilute ammonia solution with a large excess of ammonium chloride, but the amounts so obtainable areunprofitably small.

Yield: …………………..

Melting Point: ……………………

Chemical Formula and structure of Reinecke's salt:

It is a chemical compound with the formula $NH_4[Cr(NCS)_4(NH_3)_2]\cdot H_2O$. The dark-red crystalline compound is soluble in boiling water, acetone, and ethanol. The chromium atom is surrounded by six nitrogen atoms in an octahedral geometry. The NH_3 ligands are mutually *trans* and the Cr–NCS groups are linear. The salt crystallizes with one molecule of water. $NH_4[Cr(NCS)_4(NH_3)_2]$ is prepared by treatment of molten NH_4SCN (melting point around 145–150 °C) with $(NH_4)_2Cr_2O_7$.



Discussion:

Reinecke salt has been prepared by adding either potassium dichromate or ammonium dichromate to fused ammonium thiocyanate.

References and Notes:

1. Kapfhammer and Eck, Z. physiol. Chem. 170, 310 (1927); Grassmann and Lang, Biochem. Z.269, 223 (1934).
2. Reinecke, Ann. 126, 113 (1863); Christensen, J. prakt. Chem. (2) 45, 213 (1892); Zeleny and Gortner, J. Biol. Chem. 90, 430 (1931).

1. Synthesis and Characterization of inorganic compounds:

1B. $[Co(NH_3)_6]Cl_3$:

Since $CoCl_3$ is not available (the Co^{3+} would oxidise chloride to chlorine gas), $[Co(NH_3)_6]Cl_3$ is prepared from cobalt(II) chloride using a redox synthesis. The latter is treated with ammonia and ammonium chloride followed by oxidation. Oxidants include hydrogen peroxide or oxygen in the presence of charcoal catalyst.

$2CoCl_2 + 10NH_3 + 2NH_4Cl + H_2O_2 \rightarrow 2[Co(NH_3)_6]Cl_3 + 2H_2O$ ……………….. (1)

$4CoCl_2 + 4NH_4Cl + 20NH_3 + O_2 \rightarrow 4[Co(NH_3)_6]Cl_3 + 2H_2O$ ………………….(2)

$4Co(C_2H_3O_2)_2.4H_2O + 4NH_4C_2H_3O_2 + 20NH_3 + O_2 + 12HCl \rightarrow 4[Co(NH_3)_6]Cl_3 + 18H_2O + 12CH_3COOH$ …………..(3)

Experimental:

A. Chemicals:

1. Alcohol
2. Ammonia
3. Ammonium chloride
4. Hydrogen Peroxide
5. Cobalt Chloride

Apparatus:

1. Thermometer
2. Magnetic stirrer and heater
3. Suction
4. Large beaker

6.Charcoal catalyst
7.Cobalt acetate
8.Ammonium acetate

Synthesis of Reinecke Salt:

Procedure:

Eight hundred grams (10.5 moles) of ammonium thiocyanateis gently heated, by means of three small flames (Note 1), in a white enameled cooking pot of about 4-l. capacity. The mass is stirred with athermometer enclosed in a glass tube until the solid has partially melted and the temperature has reached 145–150°. At this point an intimate mixture of 170 g. (0.675 mole) of finely powdered ammoniumdichromate and 200 g. (2.6 moles) of ammonium thiocyanateis added in portions of 10–12 g. with constant stirring. After about ten such portions have been added a fairly vigorous reaction takes placewith evolution of ammonia and the temperature rises to 160°. The flames are extinguished, and the remainder of the mixture is added at such a rate that the heat of reaction maintains the temperature at 160° (Note 2). Stirring is continued while the mass cools, and any lumps of solid which form around thesides of the vessel are broken loose (Note 3).The product, while still warm (Note 4), is finely powdered and stirred with 750 cc. of ice water in a large beaker. After fifteen minutes the insoluble portion is filtered by suction, freed as completely aspossible from mother liquor without washing (Note 5), and stirred into 2.5 l. of water previouslywarmed to 65°. The temperature is then rapidly raised to 60° (Note 6), the solution is filtered at oncethrough a hot-water funnel, and the filtrate is placed in a refrigerator overnight.

The resulting crystals are collected and the mother liquor employed for a second similar extraction of the residue at 60°. This yields a further crop of crystalline Reinecke salt. The mother liquor is finallyconcentrated to 250–300 cc. by evaporation at 40–50° under reduced pressure, when a small third crop (12–13 g.) is obtained. The total yield of air-dried crystals is 250–275 g. (52–57 per cent of thetheoretical amount) (Note 7).The undissolved residue from the second extraction consists chiefly of Morland salt (the guanidine salt of the Reinecke acid) and amounts to 130–135 g. (33–34 per cent of the theoretical amount) (Note8).

NOTES

1. Heat must be applied as uniformly as possible.

2. The addition of the mixture requires five to seven minutes.

3. The product is detached from the walls during cooling as it is difficult to remove when cold.

4. The material should be pulverized while warm before it has had an opportunity to attract moisture from the air.

5. The filtrate, which consists largely of unchanged ammonium thiocyanateand its decomposition products, contains too little Reinecke salt to repay further treatment.

6. Reinecke salt decomposes in aqueous solution with formation of a blue color and free hydrogen cyanide. At room temperature this decomposition occurs in about two weeks, and above 65° it takesplace quite rapidly. A similar decomposition takes place in boiling alcohol.

7. Reinecke salt is of value as a precipitant for primary and secondary amines, prolineand hydroxyproline, and certain amino acids.1

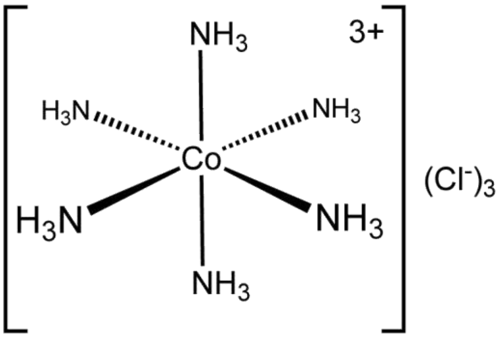
8. The Morland salt, which is soluble in acetone, contains a small proportion of a colorlesssulfur
compound insoluble in hot water. It can be partially converted into Reinecke salt by treatment in dilute ammonia solution with a large excess of ammonium chloride, but the amounts so obtainable areunprofitably small.

D. Yield: …………………..

E. Melting Point: ……………………

Chemical formula and structure of Reinecke's salt:

Hexaamminecobalt(III) chloride is the chemical compound with the formula $[Co(NH_3)_6]Cl_3$. This salt consists of $[Co(NH_3)_6]^{3+}$ cations, each accompanied by three Cl^- anions. The cation itself is a metal ammine complex with six ammonia molecules as ligands on the cobalt atom. $[Co(NH_3)_6]^{3+}$ is diamagnetic, with a low-spin $3d^6$ octahedral Co(III) center. The cation obeys the 18-electron rule and is considered to be a classic example of an exchange inert metal complex. As a manifestation of its inertness, $[Co(NH_3)_6]Cl_3$ can be recrystallized unchanged from concentrated hydrochloric acid: the NH_3 is so tightly bound to the Co(III) centers that it does not dissociate to allow its protonation. In contrast, labile metal ammine complexes, such as $[Ni(NH_3)_6]Cl_2$, react rapidly with acids, reflecting the lability of the Ni(II)–NH_3 bonds. Upon heating, hexamminecobalt(III) begins to lose some of its ammine ligands, eventually producing a stronger oxidant.



Discussion:

Reinecke salt has been prepared by adding either potassium dichromate or ammonium dichromate to fused ammonium thiocyanate.

References:

1. *Huheey, James E. (1983). Inorganic Chemistry (3rd ed.). p. 360.*
2. *Bjerrum, J.; McReynolds, J. P. (1946). "Hexamminecobalt(III) Salts". Inorg. Synth.* ***2****: 216–221. doi:10.1002/9780470132333.ch69.*
3. *Fremy, M. E. (1852). "Recherchessur le cobalt". Ann. Chim. Phys.* ***35****: 257–312.*
4. *Lindholm, R. D.; Bause, Daniel E. (1978). "Complexes of Cobalt Containing Ammonia or Ethylene Diamine: Hexaamminecobalt(III) Salts". Inorg. Synth.* ***18****: 67–69. doi:10.1002/9780470132494.ch14.*

1. Synthesis and characterization of $[Cu(NH_3)_4(SO_4)(H_2O)]$:

1C.Preparation of $[Cu(NH_3)_4(SO_4)(H_2O)]$ complex:

From a solution containing copper(II) ions insoluble basic salts can be precipitated bythe action of ammonium-hydroxide. The light blue precipitate dissolves in the excess of NH4OH, forming dark blue $[Cu(NH_3)_4]^{2+}$ complex ions. Reacting copper(II)sulfate with excess ammonium-hydroxide results in a dark blue solution, from which $[Cu(NH_3)_4]SO_4\cdot H_2O$ can be crystallized.

$$2\,CuSO_4(aq) + 2\,NH_4OH(aq) = Cu_2(OH)_2SO_4(s) + (NH_4)_2SO_4(aq)$$

$$Cu_2(OH)_2SO_4(s) + (NH_4)_2SO_4(aq) + 6\,NH_4OH(aq) = 2\,[Cu(NH_3)_4]SO_4(aq) + 8\,H_2O(l)$$

EXPERIMENTAL:

A. Chemicals:	**Apparatus:**
1. Copper sulphate	1. Mortar
2.Ammonium hydroxide	2.Magnetic stirrer and heater
3.Methanol	3.glass filter

Synthesis of $[Cu(NH_3)_4(SO_4)(H_2O)]$ complex:

Procedure:

Grind 6.2g $CuSO_4\cdot 5H_2O$ in a mortar and add it to the solution of 15 cm^3 concentrated ammoniumhydroxide and 10 cm^{3}water. In order to decrease the solubility add 15 cm^3 methanol to the solution slowly while stirring. The solution is stored for three hours in a cool place. The formed dark blue crystals are separated on a glass filter and washed with

25 $cm^3$of 1:1 mixture of methanol and NH_4OH. Finally the crystals are rinsed with methanol and dried in air stream. Since methanol is flammable, avoid working close to a flame.

NOTES

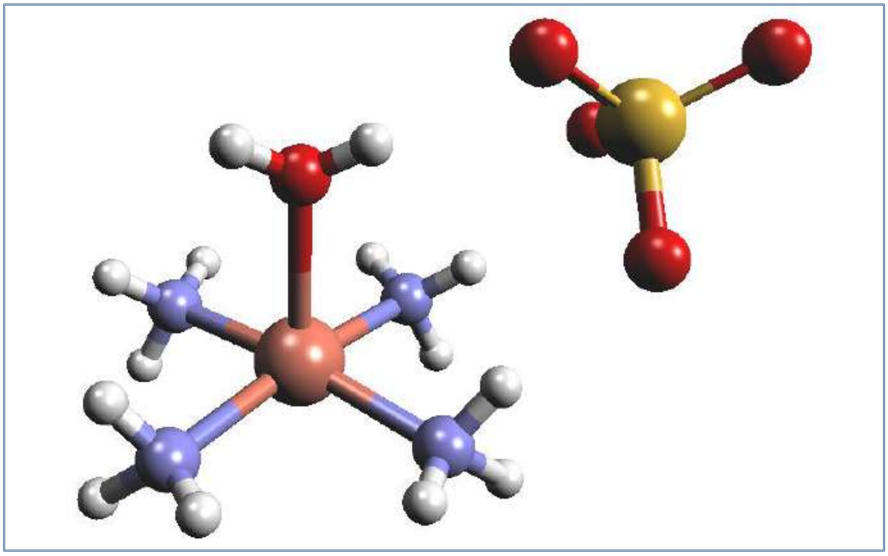
1. Heat must be applied as uniformly as possible.
2. The addition of the mixture requires five to seven minutes.
3. Separation should be done by glass filter and washed with25 $cm^3$of 1:1 mixture of methanol and NH_4OH solution.

Yield: …………………..

Melting Point: ……………………

Chemical Formula and structure of Tetraamminecopper(II) sulphate complex:

The solid state salt of tetraamminecopper(II) sulfate contains the $[Cu(NH_3)_4H_2O]SO_4$, which has a square pyramidal molecular geometry. The bond length between the atoms in the crystal are measured using X-ray crystallography; the Cu-N and Cu-O distances are about 210 and 233 pm. $Cu(NH_3)$The correct concentrations of ammonia and copper sulfate solution can be determined by colorimetry. The combination of the correct concentrations will produce the highest absorbance read out on the colorimeter and as a result the formula of the complex can be verified.



Structure of Tetraamminecopper(II) sulphate complex

Discussion:

The deep blue crystalline solid tends to hydrolyse and evolve (release) ammonia upon standing in air. It is fairly soluble in water. The brilliant dark blue-violet color of tetraamminecopper(II) sulfate solution is due to presence of $[Cu(NH_3)_4]^{2+}$. Often, the dark blue-violet color is used as a positive test to verify the presence of Cu^{2+} in a solution.

Tetraamminecopper(II) sulphate complex

References and Notes:

1. O. Glemser, H. Sauer "Tetraamminecopper (II) Sulfate" Handbook of Preparative Inorganic Chemistry, 2nd Ed., Academic Press, 1963, NY. Vol. 1. p. 1021.
2. Jump up to: American Elements – The material science company; tetraammine copper(II) sulfate monohydrate; CAS 10380-29-7
3. Morosin "The Crystal Structures of Copper Tetraammine Complexes. A. and " ActaCrystallogr. 1969, vol. B25, pp. 19-30. doi:10.1107/S0567740869001725
4. Li, Yudan; Wang, Wenjie; He, Chuan.; Chemical reduction method for preparing copper nanopowder with high purity using sodium hypophosphite as reductant, Faming ZhuanliShenqing, Dec 4, 2013, CN 103418801

1. Synthesis and Characterization of inorganic compounds:

1D. Synthesisof [Co(NH$_3$)$_5$Cl]Cl$_2$ compound:

The complex is prepared with a two-step process starting with oxidizing a solution of cobalt chloride and ammonia.

$$2\ CoCl_2{\cdot}6H_2O + 10\ NH_3 + 2\ HCl + H_2O_2 \rightarrow 2\ [Co(NH_3)_5(OH_2)]Cl_3 + 12\ H_2O$$

This intermediate is then heated to induce coordination of one of the outer sphere chloride ligands:

$$[Co(NH_3)_5(OH_2)]Cl_3 \rightarrow [Co(NH_3)_5Cl]Cl_2 + H_2O$$

Experimental:

A. Chemicals:	**Apparatus:**
1. Alcohol	1. Buchner funnel
2. Ammonia	2.Magnetic stirrer and heater
3.30% H_2O_2	3.Suction
4. Cobalt(II) chloride-hexahydrate	4. Ice bath
5. Concentrated HCl	

Preparation of [Co(NH$_3$)$_5$Cl]Cl$_2$:

Procedure:

In the fume hood, completely dissolve 6 g of NH_4Cl in ~40 mls of concentrated ammonia in a 400 ml beaker. With continuous stirring, add 12 g of cobalt(II) chloride-hexahydrate in small portions. With continued stirring of the resulting brown slurry, slowly add 10 mls of 30% H_2O_2. After the effervescence has stopped, slowly add ~30 mls of concentrated HCl. With continued stirring, heat on a hot plate and maintain 85 o C for 20 minutes. Cool mixture to room temperature in an ice bath and filter (using a Buchner funnel) the crystals of [Co(NH$_3$)$_5$Cl]Cl$_2$.

NOTES

1. Heat must be applied as uniformly as possible.
2. The addition of the mixture requires five to seven minutes.
3. The product is detached from the walls during cooling as it is difficult to remove when

cold.

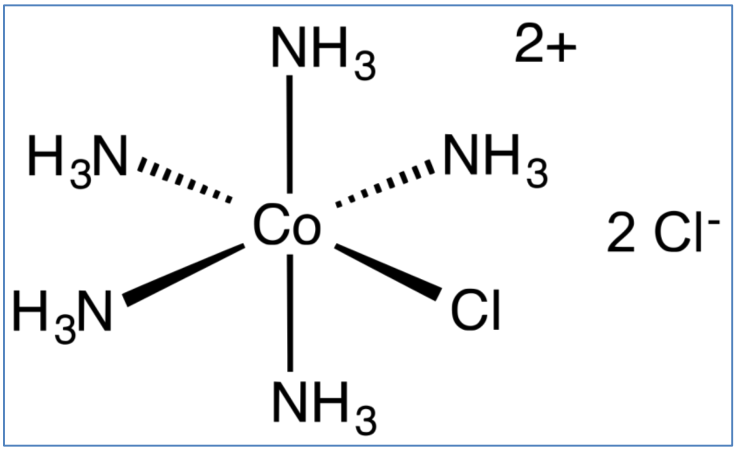
4. The material should be pulverized while warm before it has had an opportunity to attract moisture from the air.

Yield: …………………..

Melting Point: ……………………

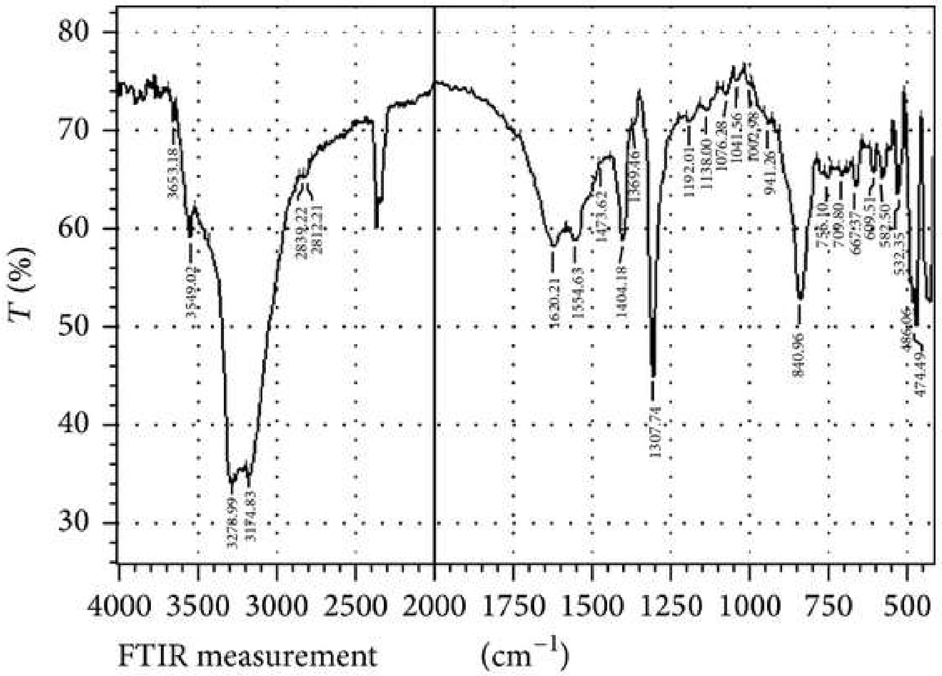
Chemical Formula and structure of $[Co(NH_3)_5Cl]Cl_2$ compound:

It is a chemical compound with the formula $[Co(NH_3)_5Cl]Cl_2$. It is a red-violet, diamagnetic, water-soluble salt. In $[Co(NH_3)_5Cl]Cl_2$, two chloride ions are outer sphere (counter ions) and one is bound to the Co(III) center: reaction with excess silver nitrate would immediately precipitate the two chloride counter ions, but the bound chloride ion would not be precipitated.



Structure of $[Co(NH_3)_5Cl]Cl_2$complex

G. Record IR spectra and interpret:



Discussion:

$[Co(NH_3)_5Cl]Cl_2$ complexhas been prepared by adding Cobalt(II) chloride-hexahydrate with ammonia.

References and Notes:

1. *Gert G. Schlessinger (1967). "Chloropentaamminecobalt(III) Chloride". Inorganic Syntheses.* ***9****: 160. doi:10.1002/9780470132401.ch43.*
2. *Williams, Gregory M; Olmsted, John, III; Preksa, Andrew P., III (1989). "Coordination complexes of cobalt: inorganic synthesis in the general chemistry laboratory". Journal of Chemical Education.* ***66****: 1043–5. doi:10.1021/ed066p1043.*
3. *G. G. Messmer; E. L. Amma (1968). "Redetermination of the crystal structure of chloropentaamminecobalt(III) dichloride". ActaCrystallogr. B.* ***24****: 417–422. doi:10.1107/S0567740868002475.*
4. *Hambley, Trevor W.; Lay, Peter A. (1986). "Comparisons of π-bonding and hydrogen bonding in isomorphous compounds: $[M(NH_3)_5Cl]Cl_2$ (M = Cr, Co, Rh, Ir, Ru, Os)". Inorganic Chemistry.* ***25****: 4553–8. doi:10.1021/ic00245a020.*
5. *Schwab, E. (8 September 2003). "Cobalt". Chemical & Engineering News.* ***81*** *(36): 80. doi:10.1021/cen-v081n036.p080.*

1. Synthesis and characterization of Potassium Trisoxalatoferrate(III) Trihydrate, $K_3[Fe(C_2O_4)_3].3H_2O$:

1E. Synthesis of $K_3[Fe(C_2O_4)_3].3H_2O$:

To prepare the complex trisoxalatoferrate(III), $Fe(C_2O_4)_3^{-3}$ anion and isolate it as its hydrated potassium salt, $K_3[Fe(C_2O_4)_3].3H_2O$. Also, to study the photochemical reduction of the sample.

THEORY:

Potassium trisoxalatoferrate(III) trihydrate, $K_3[Fe(C_2O_4)_3].H_2O$ is a green crystalline salt, soluble in hot water but rather insoluble when cold. It can be prepared by the reaction of $K_2C_2O_4.H_2O$ with $FeCl_3.6H_2O$.

$$3K_2C_2O_4.H_2O(aq) + FeCl_3.6H_2O(aq) \rightarrow K_3Fe(C_2O_4)_3].3H_2O(aq) + 3KCl(aq)$$

Experimental:

A. Chemicals:

1.$K_2C_2O_4.H_2O$
2. $FeCl_3.6H_2O$
3$K_3Fe(CN)_6$ solution
4. H_2SO_4 solution
5.distilled water

Apparatus:

1.Filterpaper
2.funnel
3. opaque objects
4.Largebeaker
5.test tubes

Synthesis of ofPotassium Trisoxalatoferrate(III) Trihydrate, $K_3[Fe(C_2O_4)_3].3H_2O$:

B. Procedure:

1. Weigh approximately 9.0 g of hydrated potassium oxalate, $K_2C_2O_4.H_2O$into a 250 mL beaker.
2. Add 30 mL of distilled water and heat to dissolve (do not boil).
3. In a second small beaker dissolve 4.4 g of $FeCl_3.6H_2O$ in a minimum amount of cold water (10-15 mL). Add the $FeCl_3.6H_2O$ solution to the warm oxalate solution and stir with a glass rod. Allow the product to crystallize (away from strong sunlight) by cooling the solution in an ice-water mixture.
4. Collect the crystalline product by filtration. The product is $K_3Fe(C_2O_4)_3].3H_2O$.

C. NOTES

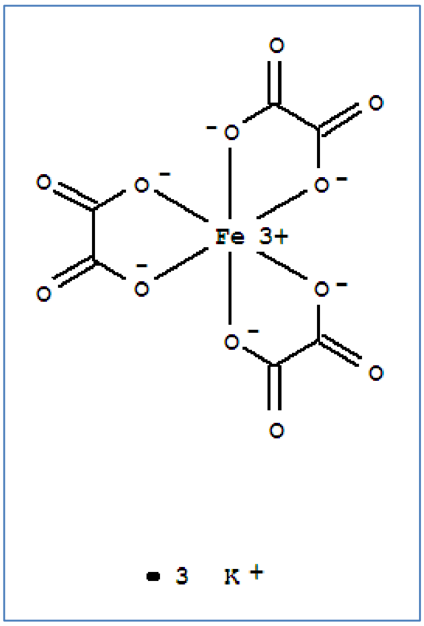
1. Heat must be applied as uniformly as possible.
2. The addition of the mixture requires five to ten minutes.
3. The product is detached from the walls during cooling as it is difficult to remove when cold.

D. Yield: …… xxxxxg.

E. Melting Point: ………yyyy……………

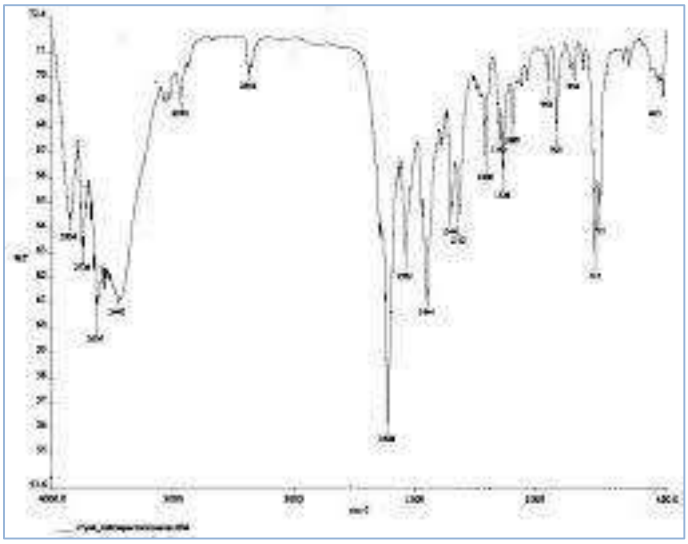
F. Chemical Formula and structure of $K_3[Fe(ox)_3]$:

It is a chemical compound with the $K_3[Fe(ox)_3]$. $K_3[Fe(C_2O_4)_3].H_2O$ is a green crystalline salt, soluble in hot water but rather insoluble when cold.The configuration of the two stereo isomeric complex ions $K_3[Fe(ox)_3]$ is described. The three oxalato groups in a complex ion are planar, their inner oxygen atoms form a slightly distorted octahedron round the central Fe atom. It is shown that both ionic and hydrogen bonds link the complex ions in the structure.



Structure of $K_3[Fe(ox)_3]$

G. Record IR spectra and interpret:



H. Discussion:

$K_3[Fe(C_2O_4)_3].H_2O$ is a green crystalline salt, soluble in hot water but rather insoluble when cold. The complex $K_3[Fe(C_2O_4)_3].H_2O$ was synthesize.The actual mass obtained was xxx g while the theoretical yield obtained was xxxg .

I. References and Notes:

1. https://pubchem.ncbi.nlm.nih.gov/compound/71310365

2. *https://www.researchgate.net/.../263032238_The_crystal_structures_of_potassium_Tris oxalato complex.*

1. Synthesis and characterization of potassium trisoxalato chromate (III) trihydrate:

1F. Synthesis of $K_3[Cr(ox)_3]$

The experiment is based on the following equation:

$$K_2Cr_2O_7 + 7H_2C_2O_4 + K_2C_2O_4\ K_3 \longrightarrow [Cr(C_2O_4)_3] + 6CO_2 + H_2O$$

Experimental:

A. Chemicals:	**Apparatus:**
1. Potassium dichromate	1. Filter paper
2.Potassium oxalate monohydrate	2. Magnetic stirrer and heater

3 Oxalic acid dihydrate
4.Potassium permanganate
5.Oxalic acid
6.Sulphuric acid
7.Sodium hydroxide
8.Silver nitrate

3. Suction
4. Large beaker

Synthesis of of potassium trisoxalato chromate (III) trihydrate:

B. Procedure:

Make a solution of potassium oxalate monohydrate (2.3 g, 12.5 mmol) and oxalic acid dihydrate (5.5 g, 43.6 mmol) in water (110-120 ml). To this solution add solid potassium dichromate (1.9 g, 6.45 mmol) in small portions with constant stirring. Concentrate the solution nearly to dryness. On cooling deep green shiny crystals of potassium tris-oxalate chromium (III) trihydrate will be formed. Filter the solid and dry by pressing between filter paper.

C. NOTES

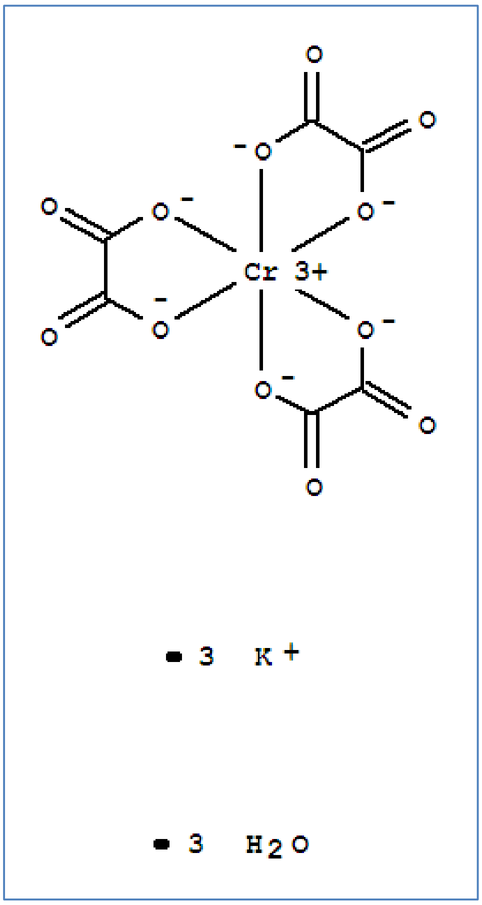
1. Heat must be applied as uniformly as possible.
2. The addition of the mixture requires five to ten minutes.
3. The product is detached from the walls during cooling as it is difficult to remove when cold.

D. Yield: …… 6.20438 g.

E. Melting Point: ……………………

F. Chemical Formula and structure of $K_3[Cr(ox)_3]$:

It is a chemical compound with the formula $K_3[Cr(ox)_3]$.The configuration of the two stereo isomeric complex ions $[Cr(C_2O_4)_3]$ is described. The three oxalato groups in a complex ion are planar, their inner oxygen atoms form a slightly distorted octahedron round the central chromium atom. It is shown that both ionic and hydrogen bonds link the complex ions in the structure.



Structure of $K_3[Cr(ox)_3]$

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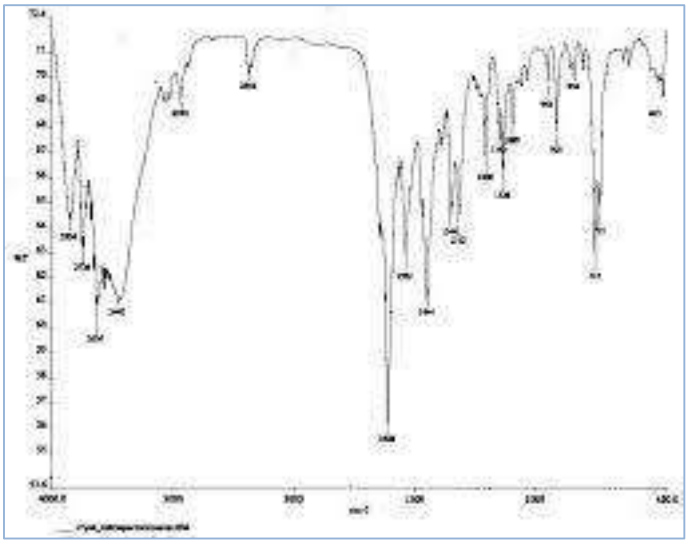


H. Discussion:

Conclusion Potassium tri(oxalato)chromium(III)trihydrate , $K_3[Cr(C_2O_4)3].3H_2O$ was synthesize.The actual mass obtained was 3.6887 g while the theoretical yield obtained was 6.20438 g .

I. References and Notes:

1. https://pubchem.ncbi.nlm.nih.gov/compound/71310365

2. *https://www.researchgate.net/.../263032238_The_crystal_structures_of_potassium_Tris oxalato complex.*

1. Synthesis and characterization $[K_2SO_4,Cr_2(SO_4)_3,24H_2O]$:

1G. Crome alum [K_2SO_4,$Cr_2(SO_4)_3$,$24H_2O$]

Potassium and chromium sulfates are directly obtained by reducing potassium dichromate with ethanol in acid medium.

$$K_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_5OH \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3CH_3CHO + 7H_2O$$

Experimental:

A. Chemicals:

1. Potassium dichromate
2.Ethanol
3Conc. Sulphuric acid 3.Suctio
4.Large beaker

Apparatus:

1. Filter paper
2.Magnetic stirrer and heater

Synthesis of ofCrome alum [K_2SO_4,$Cr_2(SO_4)_3$,$24H_2O$]:

B. Procedure:

98 grams of potassium dichromate are placed in a porcelain dish containing 400 ml of water. 76 ml of concentrated sulfuric acid are slowly added and stirred until all the salt is dissolved. If potassium dichromate has not completely dissolved the mixture is warmed gently. After all the salt has dissolved, the solution is filtered if it is not absolutely clear. Then 63 ml of ethyl alcohol are cautiously added, by stirring the reaction mixture after each addition and by allowing the heat of the reaction to raise the temperature of the solution to the boiling point. When all ethanol has been added the flask is covered and the hot solution is left to stand for a week or longer. The obtained crystals of chrome alum are filtered and if the filtrate is evaporated the additional amount of chrome alum is obtained. The crystals are dried and stored in a bottle since they are efflorescent. Chrome alum obtained by described method contains twelve molecules of crystalized water (dodecahydrate) – $KCr(SO_4)_2 \cdot 12H_2O$.

C. NOTES

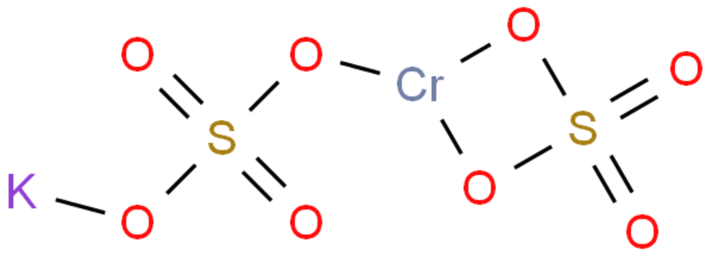
1. Heat must be applied as uniformly as possible.
2. The addition of the mixture requires five to ten minutes.
3. The crystals are dried and stored in a bottle since they are efflorescent.

D. Yield: …… **xxxx**%.

E. Melting Point: ………yyyy……………

F. Chemical Formula and structure of [K_2SO_4,$Cr_2(SO_4)_3$,24H_2O]:

It is a chemical compound with the formula [K_2SO_4,$Cr_2(SO_4)_3$,24H_2O].



Structure of [K_2SO_4,$Cr_2(SO_4)_3$,24H_2O]:

G. Discussion:

Potassium and chromium sulfates are directly obtained by reducing potassium dichromate with ethanol in acid medium. The chemical formula of chrome alum is [K_2SO_4,$Cr_2(SO_4)_3$,24H_2O].The actual mass obtained was xxx g while the theoretical yield obtained was yyyg .

H. References and Notes:

1. *Austin, George T. (1984). Shreve's Chemical process industries (5th ed.). New York: McGraw-Hill. p. 357. ISBN 9780070571471.*
2. *"Alhydrogel | Alum vaccine adjuvant for research | InvivoGen". www.invivogen.com*. Retrieved 2018-06-08.
3. *Picon, M.; et al. (2005). "L'alun des oasis occidentalesd'Egypte: researches sur terrain et recherches en laboratoire". In Borgard P.; et al. L'alun de Mediterranée.*
4. *Archontidou, A. (2005). "Un atelier de preparation de l'alun a partir de l'alunitedansl'isle de Lesbos". In Borgard P.; et al. L'alun de Mediterranée.*
5. *Hall, A. J.; Photos-Jones, E. (2005). "The nature of Melianalumen and its potential for exploitation in Antiquity". In Borgard P.; et al. L'alun de Mediterranée.*

2. Equilibrium studies on inorganic reaction:

Determination of composition of Fe(II)-1,10-phenanthroline complex in solution by Mole-Ratio method.

THEORY:

Complexation reactions of the form

$$xM + yL \leftrightarrow M_xL_y \text{…………………………..(1)}$$

are based on the reaction of a metal cation (M) and a ligand (L). These reactions are widely used in analytical chemistry. Absorption spectroscopy is a powerful tool for exploring these complexation reactions. In this experiment, two general approaches to studying the composition of complexes are used to demonstrate the necessity of carefully evaluating the properties of a particular chemical system in order to select the best method for determining the composition (metal to ligand ratio) of a complex by absorption measurements.

Mole-Ratio Method:

In this method, a series of solutions is prepared in which the concentration of one reactant is held constant while that of the other is varied. The absorbance of each solution is measured and plotted vs. the mole ratio of the reactants. Assuming the complex absorbs more than the reactants, this plot will produce an increasing absorbance up to the combining ratio. At this point, further addition of reactant will produce less increase in absorbance. Thus a break in the slope of the curve occurs at the mole ratio corresponding to the combining ratio of the complex.

REAGENTS

(i) Ferrous ammonium sulfate ($(NH_4)_2Fe(SO_4)_2\cdot6H_2O$, FW = 392.13), 7.0 x 10-4 M (250 mL)

(ii) 1,10-phenanthroline (FW = 198.23), 7.0 x 10-4 (250 mL) M

(iii) Acetic acid (17.45 M) / sodium acetate buffer, pH 4.0, total acetate = 0.01 M

(iv) Hydroxylamine hydrochloride (FW = 69.49), 5 % (w/v = g/mL) (50 mL)

PROCEDURE:

A. Solution Preparation:

Prepare the solutions listed above in the specified amounts.Make the phenanthroline solutions first. To prepare the buffer, make 250 mL of 0.01 M sodium acetate and titrate to pH 4.0 by addition of acetic acid (monitor addition with pH meter). Preparea spectroscopic blank by adding 5 mL of the acetate buffer and 1 mL of the hydroxylamine hydrochloride solution to a 25 mL volumetric flask and diluting to the mark with distilled water.

B. Absorbance Spectra of Stock Solutions.

Record the absorbance spectrum of each ofyour stock solutions vs. a distilled water reference.

D. Mole-Ratio Method.

Transfer exactly 2 mL of the standard Fe^{2+} solution to eight separate 25 mL volumetric flasks. Add 5 mL of the acetate buffer solution followed by 1 mL of the hydroxylamine hydrochloride solution. Add 2, 3, 4, 5, 6, 8, 10, and 12 mL of the 7.0 x 10-4 M 1,10-phenanthroline solution to the various flasks. Dilute to the mark with distilled water, and mix. After ten minutes measure the absorbance of each solution vs. the spectroscopic blank. Make three replicate absorbance measurements.

CALCULATIONS

Sections 1 below produce plots with linear portions that intersect. For each plot, associate each point with either the left or right linear portions and perform two least-squares calculations to estimate the linear equations (y = mx + b) that represent the left and right linear portions of the plot. Slopes, intercepts, and values of r2 should be tabulated for each of these least-squares calculations.The intersections of the lines can be found mathematically by finding the point on the x- axis where the lines have the same y-value (i.e., setting the equations equal to each other andsolving for x). If replicate absorbance measurements have been made, all plots should haveerror bars based on the 95% confidence intervals of the absorbance measurements.
1. For the mole-ratio method, plot absorbance vs. moles of reagent/mole of iron. Extrapolate the linear portions of the graph and locate the intersection by use of the mathematical procedure described above.2. Postulate the formula for the complex and draw its structure. In the discussion section ofyour report, comment on any discrepancies between the combining ratios suggested by thetwo measurement approaches.

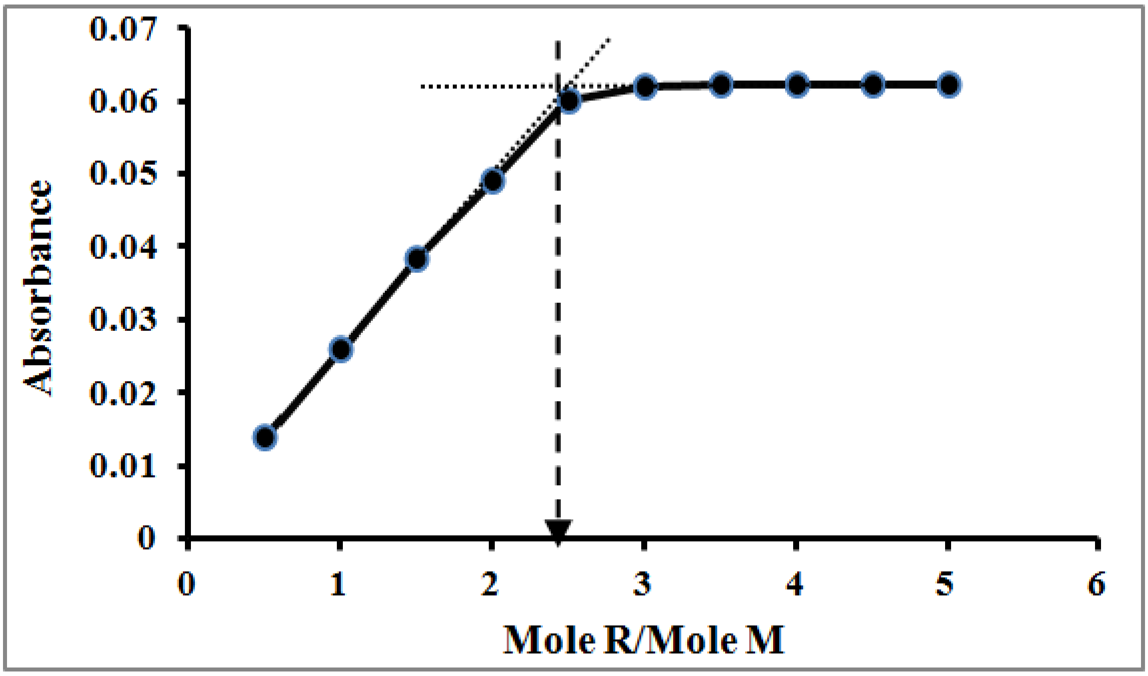


Figure 1. Mole-ratio plots for 1:3 complexe.

REFERENCES

1. W. C. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.* **1941**, *63*, 437.
2. D. A. Skoog, D. M. West, F. J. Holler, *Fundamentals of Analytical Chemistry*, 5th Ed.; Saunders: New York, 1988; pp. 525-528.

3. Spectrophotometric Estimation:

Colourimetric estimation of Fe(III) (as thiocyanate complex)

Aim: To determine the mass of ferric iron present in the whole of the given solution colourimetrically as the thiocyanate complex.

Principle:

When treated with excess of thiocyanate ions, ferric salt solutions produce red colour proportional to the amount of iron present.

$$Fe^{3+} + 6CNS^{-} \rightarrow [Fe(CNS)_6]^{3-}$$

A calibration curve can be obtained by plotting the absorbance against concentration for a set of standard solutions after developing the colour using thiocyanate. The concentration of an unknown solution can then be obtained by developing its colour under similar conditions and measuring its absorbance. The colour fades with time due to reduction of ferric iron by thiocyanate ions. Therefore readings have to be taken immediately after developing the colour.

Chemicals required:

(1) Ferric alum [$NH_4Fe(SO_4)_2$ $12H_2O$; molar mass =482.2] – 1 g.

(2) approx. 5 N HCl (iron-free) - 100 cm^3.

(3) 20% amm. thiocyanate solution - 100 cm^3.

Apparatus required:

(1) Ten 100 cm^3 volumetric flasks.

(2) 10 cm^3 graduated pipette.

(3) Funnel, beaker.

(4) Photoelectric colourimeter / spectrophotometer.

Procedure:

(*Note: Colours are developed in the solutions for calibration and estimation simultaneously. Switch on the colourimeter at least 30 minutes before use. Set zero using the blank solution. Do not switch off or change settings till all readings are taken*)

A standard iron solution containing 0.1 mg iron per milliliter is prepared as follows: 0.8634 g ferric alum is weighed into a 100 cm3 volumetric flask. 10cm^{3}of conc. HCl (iron-free) is added to prevent hydrolysis. It is then made up to 100 cm^3. 10 cm^3 of this solution is pipetted into another volumetric flask and made up to 100 cm^3. This solution now contains 0.1 mg iron per milliliter. Transfer the given solution quantitatively into a 100 cm3 volumetric flask and make up to the mark using distilled water. 2, 4, 6, 8 and 10 cm3 of standard iron solution are taken in 5 different 100 cm3 volumetric flasks. 10 cm3 of distilled water is taken in another volumetric flask to be used as blank to set the spectrophotometer. Two suitable volumes (say 4 cm3 and 6 cm3) of the given solution are also taken in two other volumetric flasks. 5 cm3 of

5 N HCl and 5 cm3 of 20% amm. thiocyanate solution are added to each and made up to 100 cm3. The absorbances are measured at 480 nm. Plot the absorbance against volume of standard iron solution to obtain the calibration curve. Using the absorbance values for the given solution, find the corresponding volume equivalent to the standard iron solution from the calibration curve. Mass of iron in this volume and hence mass of iron in the whole of the given solution is then computed.

Result:

Mass of iron in the whole of the given solution = (1) ________________ g.
(2) ________________ g.

Calculation:

Calibration:

Mass of ferric alum weighed = w g.

Therefore, mass of iron per cm^3 of standard solution, (m) = (0.1 / 0.864) × w mg.

Estimation:

Volume of made up solution used for colour development = v cm^3.

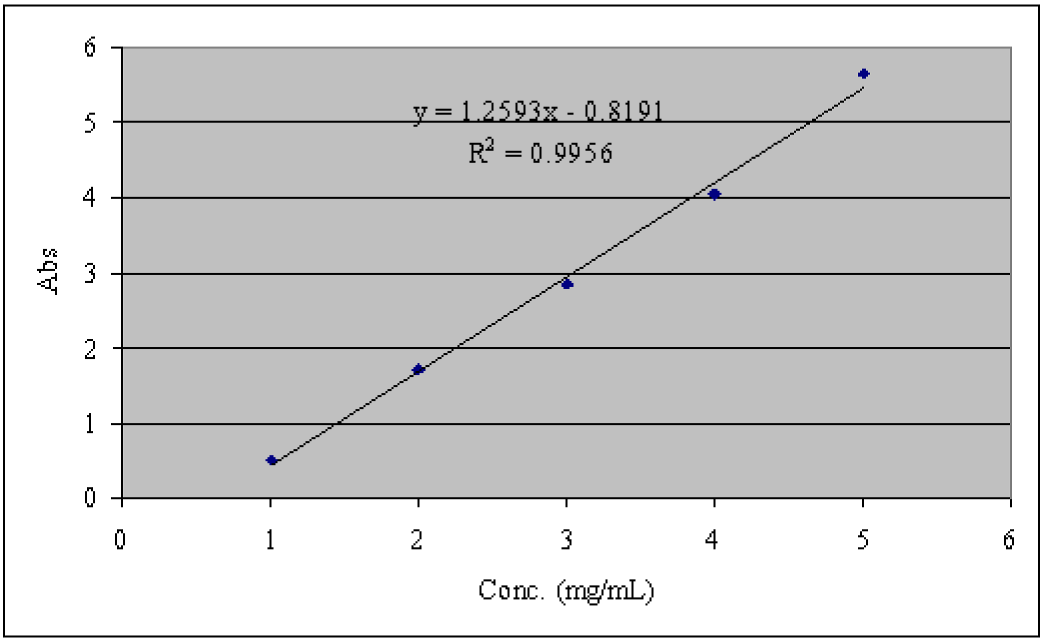
Volume corresponding to standard solution from graph = V cm^3.

Mass of iron corresponding to V cm^3.standard = V.m = x mg.

Mass of iron corresponding to v cm^3 = x mg.

Therefore, Mass of iron in the whole of the given solution = (x / v) ×100 mg.

*(**Note to instructor**: Solution remaining from the first 100* cm^3 *of standard solution can be used for giving unknown to students. Give a volume between 8* cm^3*and 12* cm^3 *from this for estimation to each student.)*



4. Quantitative analysis:

4A. Gravimetric estimation of Ni(II) as Ni(DMGH$)_2$

Objectives:

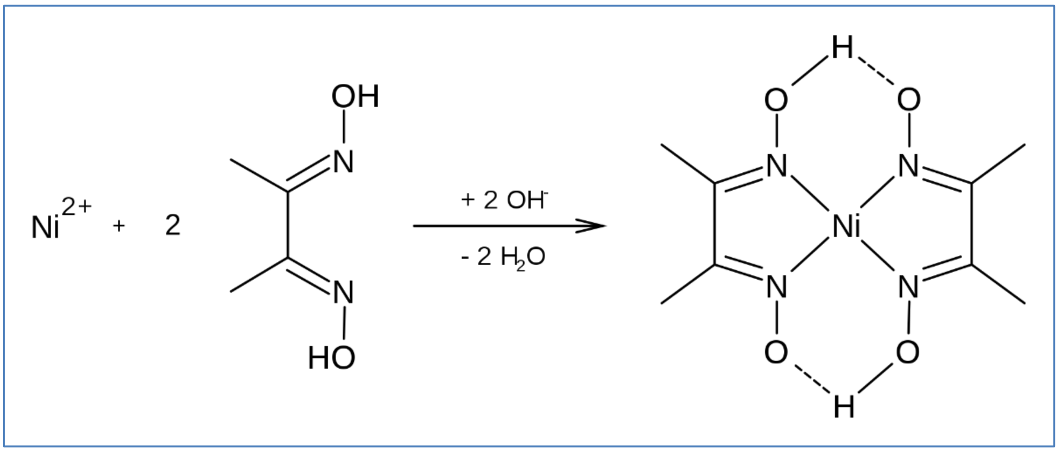
- To precipitate nickel from the solution by adding dimethyl glyoxime.
- Filtration of precipitate using sintered glass crucible.
- Mass of nickel calculated from the mass of precipitate.

Theory:

Gravimetric analysis is one of the most accurate analytical methods available. It is concerned with the determination of a substance by the process of weighing. The element or radical to be determined is converted into a stable compound of definite composition and the mass of the compound is determined accurately. From this, the mass of element or radical is calculated.The gravimetric analysis involves a) precipitation b) filtration c) washing of the precipitate and d) drying, ignition and weighing of the precipitate. Nickel ion can be estimate quantitatively by precipretating nickel as the nickel dimethyl glyoximate complex.

The nickel is precipitated as nickel dimethyl glyoxime by adding alcoholic solution of dimethyl glyoxime$C_4H_6(NOH)_2$ and then adding a slight excess of aqueous ammonia solution.

$$NiSO_4 + 2\,C_4H_8O_2N_2 \longrightarrow Ni(C_4H_7O_2N_2)_2 + H_2SO_4$$



nickel bis(dimethylglyoximate) complex

Chemicals required:

(1) Nickel sulphate (3gm)

(2) Dimethylglyoxime

(3) Hydro chloric acid

Apparatus required:

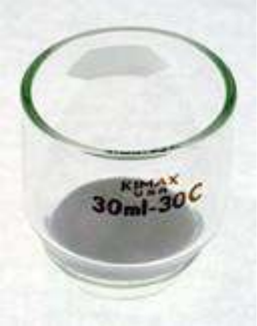
(1) Ten 100 cm^3 volumetric flasks.

(2) 10 cm^3 graduated pipette.

(3) Funnel, beaker.

(4) Goch crucible

(5) glass rod



Goch crucible

Procedure:

The steps commonly followed in gravimetric analysis are;

(1) Preparation of a solution containing a known weight of the sample.

(2) Separation of the desired constituent.

(3) Weighing the isolated constituent.

(4) Computation of the amount of the particular constituent in the sample from the observed weight of the isolated substance.

When the pH is buffered in the range of 5 to 9, the formation of the red chelate occurs quantitatively in a solution. The chelation reaction occurs due to donation of the electron pairs on the four nitrogen atoms, not by electrons on the oxygen atoms. The reaction is performed in a solution buffered by either an ammonia or citrate buffer to prevent the pH of the solution from falling below 5. If the pH does become too low the equilibrium of the above reaction favors the formation of the nickel (II) ion, causing the dissolution of Ni (DMG)2 back into the mother liquor.

A slight excess of the reagent has no action on the precipitate, but a large excess should be avoided because of the possible precipitation of the reagent itself. The precipitate is soluble in the free mineral acids. It is therefore crucial to avoid the addition of too large and excess of the reagent because it may crystallize out with the chelate. It is also important to know that the complex itself is slightly soluble to some extent in alcoholic solutions. By adding small amount of chelating agents will minimize the errors from these sources. The amount of the reagent added is also governed by the presence of other metals such as cobalt, which form soluble complexes with the reagent. If a high quantity of these ions is present, a greater amount of DMG must be added. The nickel dimethylglyoximate is a very bulky precipitate. Therefore, the sample weight used in the analysis must be carefully controlled to allow more convenient handling of the precipitate during the transfer to the filtering crucible. The compactness of the precipitate is improved by adjusting the pH to 3 or 4, followed by the addition of ammonia solution.

A slow increase in the concentration of ammonia in the solution causes a slight increase in the pH gradually and results in the precipitation of the complex. The result is the formation of a denser precipitate. Once the filtrate has been collected and dried, the nickel content of the solution is calculated stoichiometrically from the weight of the precipitate.

Ni-DMG Complex

Result:

Weight of Goch crusible constant(w_1)	**Weight after drying(w_2)**

Calculation:

Weight of Goch crusible constant(W_1) = xxx gm

Weight of Goch crusible constant + Nickel dimethyl glyoximate complex =W_2= yyy gm.

Therefore, Weight ofNickel dimethyl glyoximate complex = (W_2 - W_1) gm

$$\underset{288.69}{Ni(C_4H_7O_2N_2)_2} \equiv \underset{59.69}{Ni}$$

288.91 g nickeldimethylglyoximate contains = 58.69 g of nickel

So, X g of nickeldimethylglyoximate contains = 58.69/288.91 x X

Or, 25 ml of the solution contains = 58.69/288.91 x X g of nickel

1000 ml of the given solution contains = 58.69 / 288.91 x X x 1000/25 g

Therefore, weight of Ni in 1000 ml of the given solution contains

$$\equiv \frac{(W2 - W1)\ gm}{288.89} X\ 59.69\ X \frac{1000}{25} = ??$$

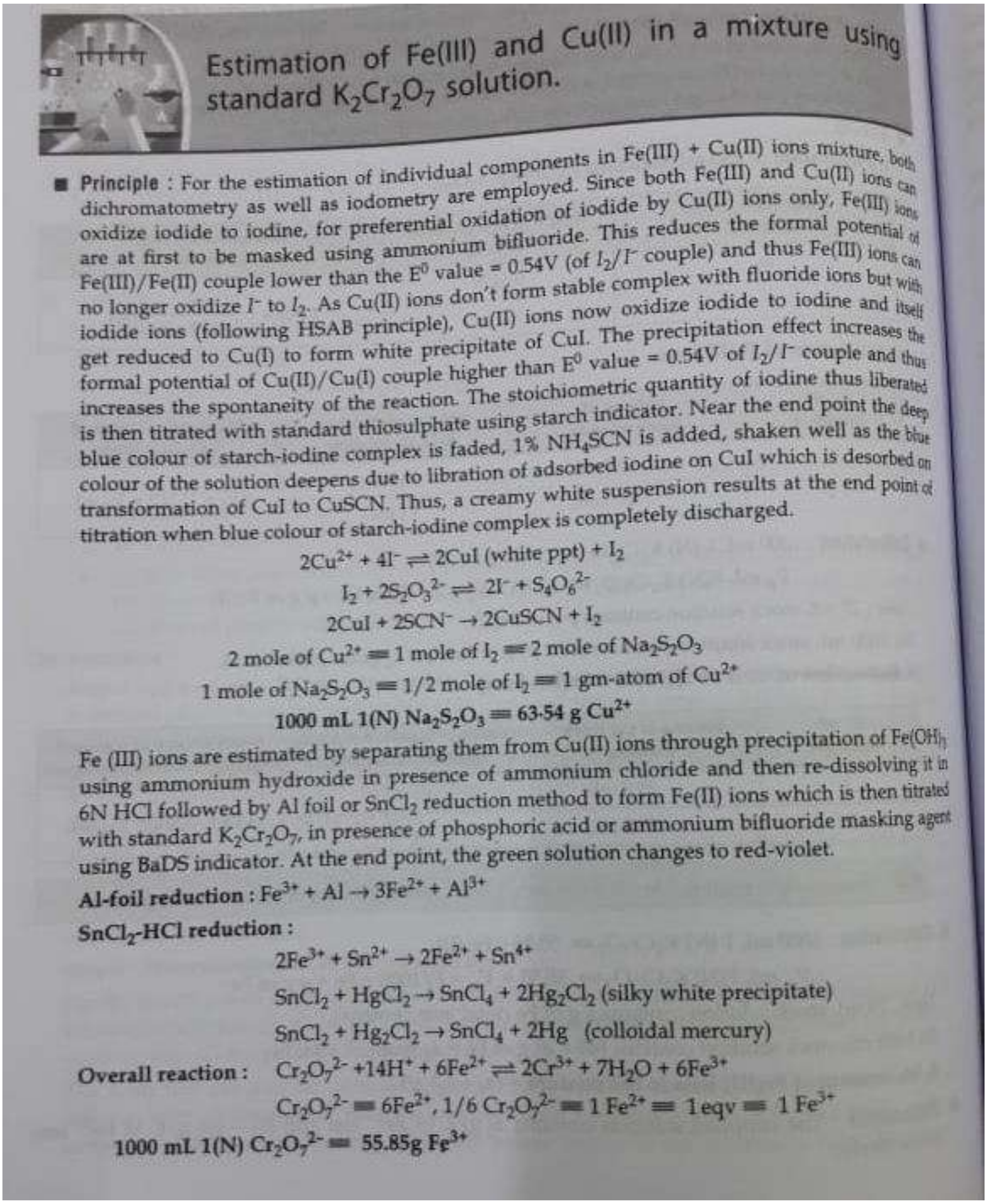
……………………………………………………………………………………………………

References

1. *Semon, W. L.; Damerell, V. R. (1930). "Dimethylglyoxime". Organic Syntheses.* ***10****: 22. doi:10.15227/orgsyn.010.0022.*
2. *Lev Tschugaeff (1905). "Übereinneues, empfindlichesReagens auf Nickel". Berichte der deutschenchemischenGesellschaft.* ***38*** *(3): 2520–2522.doi:10.1002/cber.19050380317.*

3. *Girolami, G.. S.; Rauchfuss, T.B.; Angelici, R. J. (1999). Synthesis and Technique in Inorganic Chemistry: A Laboratory Manual (3rd ed.). pp. 213–215.*

Experiment 4B: Estimation of Fe (III) and Cu(II) in a mixture using $K_2Cr_2O_7$.



Estimation of Fe(III) and Cu(II) in a mixture using standard $K_2Cr_2O_7$ solution.

- **Principle** : For the estimation of individual components in Fe(III) + Cu(II) ions mixture, both dichromatometry as well as iodometry are employed. Since both Fe(III) and Cu(II) ions can oxidize iodide to iodine, for preferential oxidation of iodide by Cu(II) ions only, Fe(III) ions are at first to be masked using ammonium bifluoride. This reduces the formal potential of Fe(III)/Fe(II) couple lower than the E^0 value = 0.54V (of I_2/I^- couple) and thus Fe(III) ions can no longer oxidize I^- to I_2. As Cu(II) ions don't form stable complex with fluoride ions but with iodide ions (following HSAB principle), Cu(II) ions now oxidize iodide to iodine and itself get reduced to Cu(I) to form white precipitate of CuI. The precipitation effect increases the formal potential of Cu(II)/Cu(I) couple higher than E^0 value = 0.54V of I_2/I^- couple and thus increases the spontaneity of the reaction. The stoichiometric quantity of iodine thus liberated is then titrated with standard thiosulphate using starch indicator. Near the end point the deep blue colour of starch-iodine complex is faded, 1% NH_4SCN is added, shaken well as the blue colour of the solution deepens due to libration of adsorbed iodine on CuI which is desorbed on transformation of CuI to CuSCN. Thus, a creamy white suspension results at the end point of titration when blue colour of starch-iodine complex is completely discharged.

$$2Cu^{2+} + 4I^- \rightleftharpoons 2CuI\ (\text{white ppt}) + I_2$$

$$I_2 + 2S_2O_3^{2-} \rightleftharpoons 2I^- + S_4O_6^{2-}$$

$$2CuI + 2SCN^- \rightarrow 2CuSCN + I_2$$

$$2\text{ mole of } Cu^{2+} \equiv 1\text{ mole of } I_2 \equiv 2\text{ mole of } Na_2S_2O_3$$

$$1\text{ mole of } Na_2S_2O_3 \equiv 1/2\text{ mole of } I_2 \equiv 1\text{ gm-atom of } Cu^{2+}$$

$$\mathbf{1000\ mL\ 1(N)\ Na_2S_2O_3 \equiv 63{\cdot}54\ g\ Cu^{2+}}$$

Fe (III) ions are estimated by separating them from Cu(II) ions through precipitation of $Fe(OH)_3$ using ammonium hydroxide in presence of ammonium chloride and then re-dissolving it in 6N HCl followed by Al foil or $SnCl_2$ reduction method to form Fe(II) ions which is then titrated with standard $K_2Cr_2O_7$, in presence of phosphoric acid or ammonium bifluoride masking agent using BaDS indicator. At the end point, the green solution changes to red-violet.

Al-foil reduction : $Fe^{3+} + Al \rightarrow 3Fe^{2+} + Al^{3+}$

$SnCl_2$-HCl reduction :

$$2Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$$

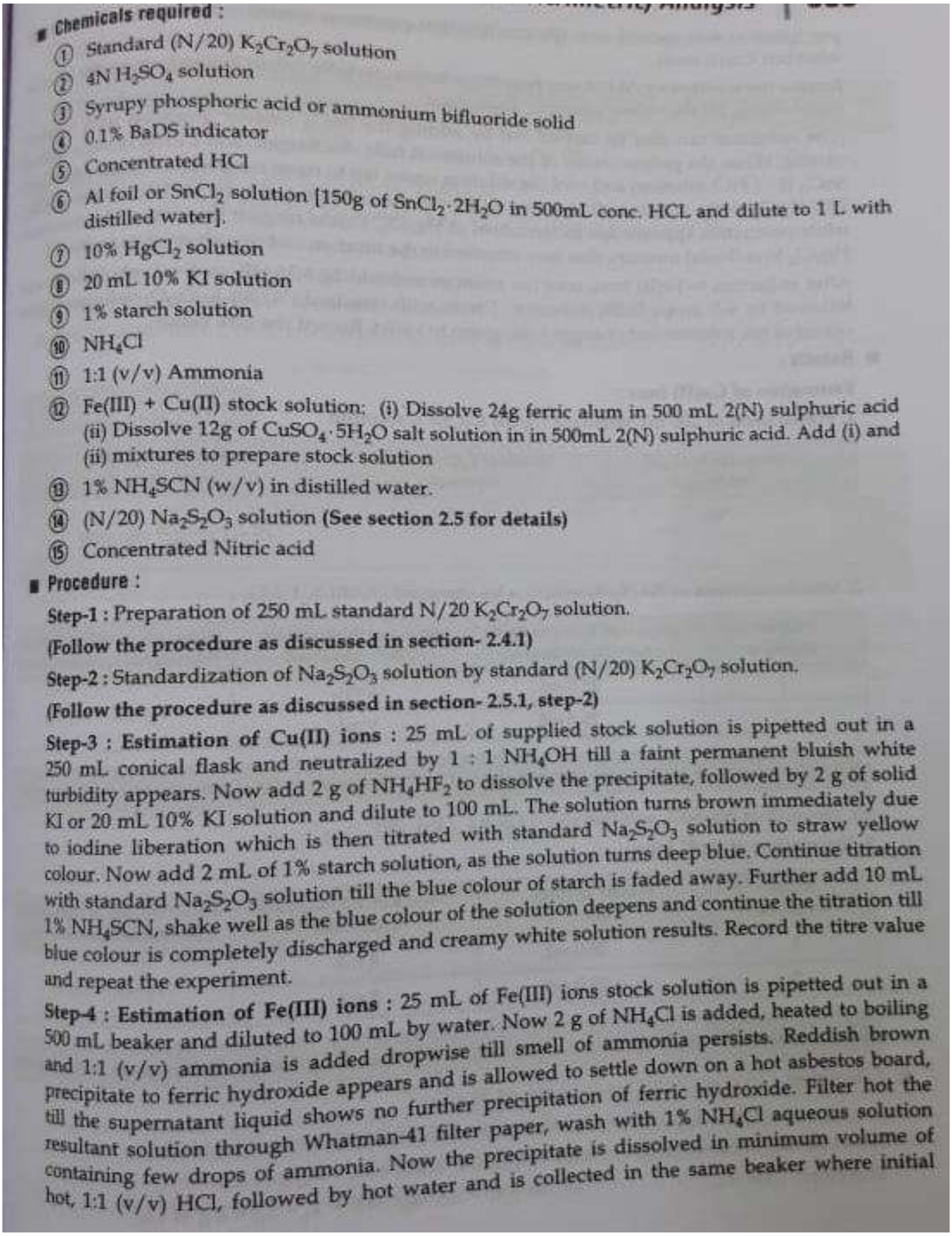
$$SnCl_2 + HgCl_2 \rightarrow SnCl_4 + 2Hg_2Cl_2\ (\text{silky white precipitate})$$

$$SnCl_2 + Hg_2Cl_2 \rightarrow SnCl_4 + 2Hg\quad (\text{colloidal mercury})$$

Overall reaction : $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightleftharpoons 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

$$Cr_2O_7^{2-} \equiv 6Fe^{2+},\ 1/6\ Cr_2O_7^{2-} \equiv 1\ Fe^{2+} \equiv 1\text{ eqv} \equiv 1\ Fe^{3+}$$

$$\mathbf{1000\ mL\ 1(N)\ Cr_2O_7^{2-} \equiv 55.85g\ Fe^{3+}}$$



Chemicals required :

① Standard (N/20) $K_2Cr_2O_7$ solution
② 4N H_2SO_4 solution
③ Syrupy phosphoric acid or ammonium bifluoride solid
④ 0.1% BaDS indicator
⑤ Concentrated HCl
⑥ Al foil or $SnCl_2$ solution [150g of $SnCl_2 \cdot 2H_2O$ in 500mL conc. HCL and dilute to 1 L with distilled water].
⑦ 10% $HgCl_2$ solution
⑧ 20 mL 10% KI solution
⑨ 1% starch solution
⑩ NH_4Cl
⑪ 1:1 (v/v) Ammonia
⑫ Fe(III) + Cu(II) stock solution: (i) Dissolve 24g ferric alum in 500 mL 2(N) sulphuric acid (ii) Dissolve 12g of $CuSO_4 \cdot 5H_2O$ salt solution in in 500mL 2(N) sulphuric acid. Add (i) and (ii) mixtures to prepare stock solution
⑬ 1% NH_4SCN (w/v) in distilled water.
⑭ (N/20) $Na_2S_2O_3$ solution **(See section 2.5 for details)**
⑮ Concentrated Nitric acid

Procedure :

Step-1 : Preparation of 250 mL standard N/20 $K_2Cr_2O_7$ solution.

(Follow the procedure as discussed in section- 2.4.1)

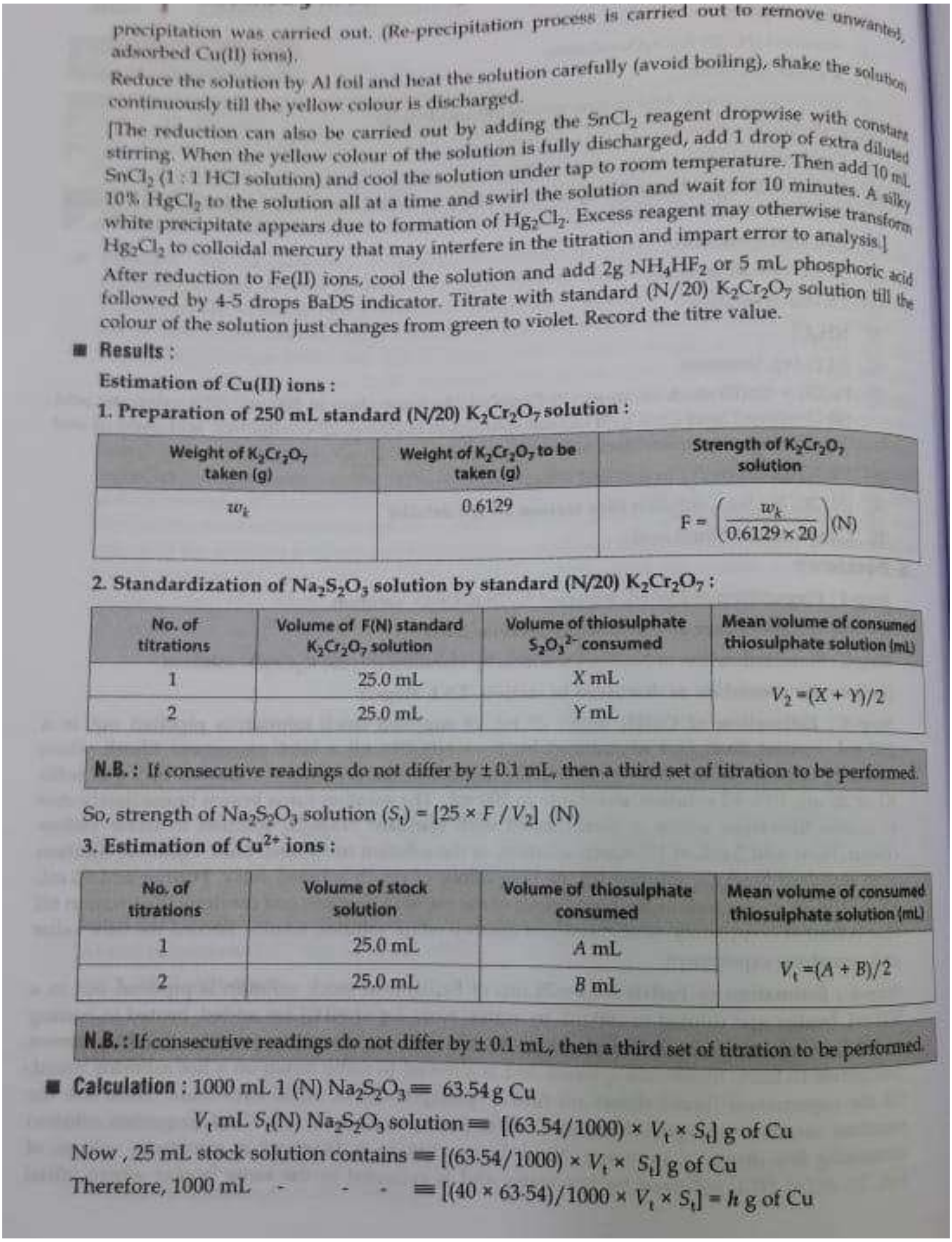
Step-2 : Standardization of $Na_2S_2O_3$ solution by standard (N/20) $K_2Cr_2O_7$ solution.

(Follow the procedure as discussed in section- 2.5.1, step-2)

Step-3 : Estimation of Cu(II) ions : 25 mL of supplied stock solution is pipetted out in a 250 mL conical flask and neutralized by 1 : 1 NH_4OH till a faint permanent bluish white turbidity appears. Now add 2 g of NH_4HF_2 to dissolve the precipitate, followed by 2 g of solid KI or 20 mL 10% KI solution and dilute to 100 mL. The solution turns brown immediately due to iodine liberation which is then titrated with standard $Na_2S_2O_3$ solution to straw yellow colour. Now add 2 mL of 1% starch solution, as the solution turns deep blue. Continue titration with standard $Na_2S_2O_3$ solution till the blue colour of starch is faded away. Further add 10 mL 1% NH_4SCN, shake well as the blue colour of the solution deepens and continue the titration till blue colour is completely discharged and creamy white solution results. Record the titre value and repeat the experiment.

Step-4 : Estimation of Fe(III) ions : 25 mL of Fe(III) ions stock solution is pipetted out in a 500 mL beaker and diluted to 100 mL by water. Now 2 g of NH_4Cl is added, heated to boiling and 1:1 (v/v) ammonia is added dropwise till smell of ammonia persists. Reddish brown precipitate to ferric hydroxide appears and is allowed to settle down on a hot asbestos board, till the supernatant liquid shows no further precipitation of ferric hydroxide. Filter hot the resultant solution through Whatman-41 filter paper, wash with 1% NH_4Cl aqueous solution containing few drops of ammonia. Now the precipitate is dissolved in minimum volume of hot, 1:1 (v/v) HCl, followed by hot water and is collected in the same beaker where initial

]



precipitation was carried out. (Re-precipitation process is carried out to remove unwanted, adsorbed Cu(II) ions).

Reduce the solution by Al foil and heat the solution carefully (avoid boiling), shake the solution continuously till the yellow colour is discharged.

[The reduction can also be carried out by adding the $SnCl_2$ reagent dropwise with constant stirring. When the yellow colour of the solution is fully discharged, add 1 drop of extra diluted $SnCl_2$ (1 : 1 HCl solution) and cool the solution under tap to room temperature. Then add 10 mL 10% $HgCl_2$ to the solution all at a time and swirl the solution and wait for 10 minutes. A silky white precipitate appears due to formation of Hg_2Cl_2. Excess reagent may otherwise transform Hg_2Cl_2 to colloidal mercury that may interfere in the titration and impart error to analysis.]

After reduction to Fe(II) ions, cool the solution and add 2g NH_4HF_2 or 5 mL phosphoric acid followed by 4-5 drops BaDS indicator. Titrate with standard (N/20) $K_2Cr_2O_7$ solution till the colour of the solution just changes from green to violet. Record the titre value.

- **Results :**

Estimation of Cu(II) ions :

1. Preparation of 250 mL standard (N/20) $K_2Cr_2O_7$ solution :

Weight of $K_2Cr_2O_7$ taken (g)	Weight of $K_2Cr_2O_7$ to be taken (g)	Strength of $K_2Cr_2O_7$ solution
w_k	0.6129	$F = \left(\frac{w_k}{0.6129 \times 20}\right)$(N)

2. Standardization of $Na_2S_2O_3$ solution by standard (N/20) $K_2Cr_2O_7$:

No. of titrations	Volume of F(N) standard $K_2Cr_2O_7$ solution	Volume of thiosulphate $S_2O_3^{2-}$ consumed	Mean volume of consumed thiosulphate solution (mL)
1	25.0 mL	X mL	$V_2 = (X + Y)/2$
2	25.0 mL	Y mL	

N.B. : If consecutive readings do not differ by ± 0.1 mL, then a third set of titration to be performed.

So, strength of $Na_2S_2O_3$ solution $(S_t) = [25 \times F / V_2]$ (N)

3. Estimation of Cu^{2+} ions :

No. of titrations	Volume of stock solution	Volume of thiosulphate consumed	Mean volume of consumed thiosulphate solution (mL)
1	25.0 mL	A mL	$V_t = (A + B)/2$
2	25.0 mL	B mL	

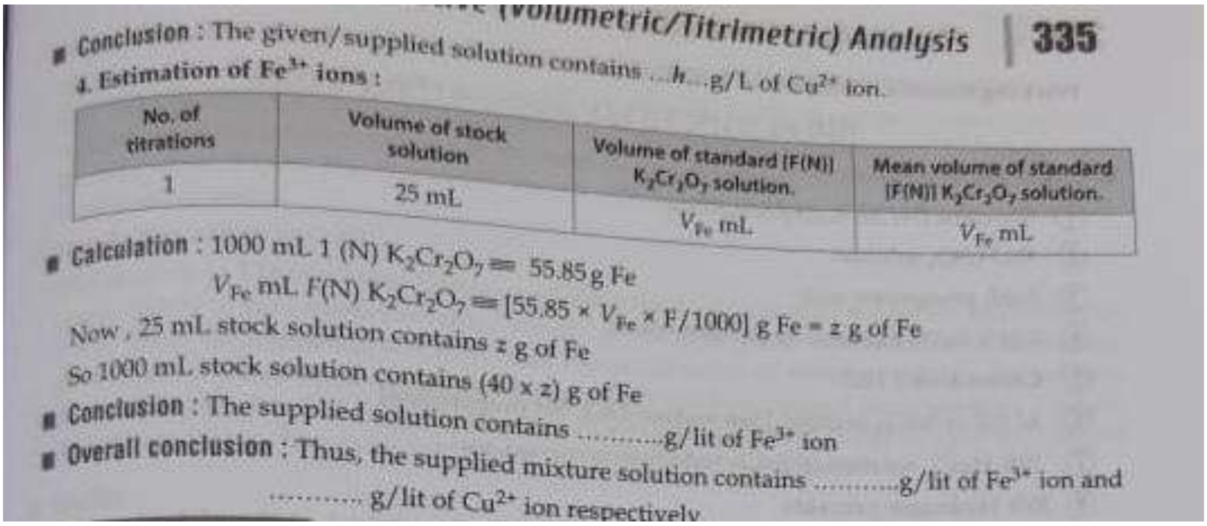
N.B. : If consecutive readings do not differ by ± 0.1 mL, then a third set of titration to be performed.

- **Calculation :** 1000 mL 1 (N) $Na_2S_2O_3 \equiv$ 63.54 g Cu

V_t mL S_t(N) $Na_2S_2O_3$ solution $\equiv [(63.54/1000) \times V_t \times S_t]$ g of Cu

Now , 25 mL stock solution contains $\equiv [(63{\cdot}54/1000) \times V_t \times S_t]$ g of Cu

Therefore, 1000 mL - - - $\equiv [(40 \times 63{\cdot}54)/1000 \times V_t \times S_t] = h$ g of Cu



(Volumetric/Titrimetric) Analysis 335

- **Conclusion :** The given/supplied solution contains ...h...g/L of Cu^{2+} ion.

4. Estimation of Fe^{3+} ions :

No. of titrations	Volume of stock solution	Volume of standard (F(N)) $K_2Cr_2O_7$ solution.	Mean volume of standard (F(N)) $K_2Cr_2O_7$ solution.
1	25 mL	V_{Fe} mL	V_{Fe} mL

- **Calculation :** 1000 mL 1 (N) $K_2Cr_2O_7 \equiv$ 55.85 g Fe

  V_{Fe} mL F(N) $K_2Cr_2O_7 \equiv [55.85 \times V_{Fe} \times F/1000]$ g Fe = z g of Fe

Now , 25 mL stock solution contains z g of Fe

So 1000 mL stock solution contains (40 x z) g of Fe

- **Conclusion :** The supplied solution contains ....g/lit of Fe^{3+} ion
- **Overall conclusion :** Thus, the supplied mixture solution contains ....g/lit of Fe^{3+} ion and .... g/lit of Cu^{2+} ion respectively

Experiment 4C. Gravimetric estimation of Zn(II) as $Zn(NH_4)(PO_4)$

Principle

The test solution zinc is first treated diammonium hydrogen phosphate solution to precipitate zinc as zinc ammonium phosphate

$$ZnC1_2(aq) + (NH_4)_2HPO_4(aq) \rightarrow ZnNH_4PO_4(s) + HCl(aq)$$

The precipitate is filtered, washed, dried and weighed. By knowing the mass of $ZnNH_4P0_4$ formed, we can calculate the concentrations of zinc chloride in the solution.

Requirements

You will need the following apparatus, chemicals and solutions for this experiment:

Chemicals	**Apparatus**
10% Ammonium thiocyanate	Beaker 500 cm3 Beaker 250 cm3
Aqueous ammonia	Bunsen burner
10% Diamrnonium hydrogen phosphate	Desiccator Filtration apparatus
Conc. Hydrochloric acid	Water bath
Methyl red indicator	Wash bottle Watch glass
Conc. Nitric acid	Sintered crucible (G-4) Tripod stand
Ammonium hydrogen sulphite solution Test Solution	Flask conical 250 cm3 Glass rod Pair of tongs

PROCEDURE

I. To the supplied compound add 100 cm3 of distilled water and dissolve the contents by shaking. Add 2-3 drops of methyl red indicator and then add 10% aqueous ammonia solution till smell of ammonia prevails and the colour of the methyl red changes to yellow.

II. To the solution obtained in step I, add slowly 10% diammonium hydrogen phosphate with adequate stirring with a glass rod. Digest the precipitate on a water bath atleast for **30** minutes.

III. Filter the precipitate, obtained in step II, through a previously weighed sintered crucible of porosity G-4. Drain out the supernatant liquid first and then the precipitate with minimum quantity of liquid.

IV. Wash the precipitate with 2-3% diammonium hydrogen phosphate (DAI-IP) solution. Finally wash the precipitate with 50% alcohol to remove the excess of DAHP. Check if any phosphate ions are present in the washings.

V. Heat the crucible and the precipitate at temperature range 100- 120'~ in an hot air oven. Cool the crucible in a desiccator and then weigh it. Repeat heating, cooling and weighing till a constant mass of the cru~iblew ith precipitate is obtained.

OBSERVATIONS

1st mass of empty crucible = ... g

2nd mass of empty crucible = ... g

1st mass of crucible + $ZnNH_4PO_4$ = ... g

2nd mass of crucible + $ZnNH_4PO_4$ = ... g

CALCULATIONS

Mass of $ZnNH_4PO_4$ obtained = viii) – vi) =........... g $= w'$ g

From stoichiometry we know

$$ZnCl_2 \equiv Zn^{2+} \equiv ZnNH_4PO_4$$

$$136.37\ g \equiv 65.37\ g \equiv 178.34\ g$$

Hence, w' g of $ZnNH_4PO_4 \equiv \frac{136.37 \times w'}{178.34}$ g of $ZnCl_2$

This much $ZnCl_2$ is present in 50 cm^3 of test solution.

Hence, concentration of $ZnCl_2$ in test solution

$$= \frac{136.37 \times w' \times 1000}{178.34 \times 50}\ g\ dm^{-3}$$

$$\boxed{\text{Concentration of } ZnCl_2 = \frac{136.37 \times 1000 \times \text{ mass of } ZnNH_4PO_4}{178.34 \times \text{ Volume of test solution}}\ g\ dm^{-3}}$$

RESULT

You can report your result in the following manner:

Concentration of zinc chloride in the test solution = ... g dm^{-3}

Experiment 4D. Gravimetric estimation of Cu(II) as CuSCN

Gravimetric analyses belong to the most precise, because contemporary analytical balances make possible determination of the mass of a sample with great accuracy. In these analyses one should obtain high purity compound of the analyzed element or a compound directly obtained from the analyzed substance). This reaction has to be exactly stoichiometric. It is also important that the weighed compound was non-hydroscopic and stable in air, it also better if it has relatively high molecular mass, because in this case the weighing is more precise. Examples of gravimetric analyses of high precision and still often used in practice are, among others:

Analysis of iron precipitated as $Fe(OH)_3$ and heated in electric oven at ca. 800ºC to oxide Fe_2O_3; Analysis of barium precipitated as BaSO4 (or analysis of sulfates precipitated by Ba2+ salts), the precipitate is heated to ca. 500ºC.

Copper will be precipitated as CuSCN (solubility product Ksp=12.7). This means that Cu^{2+} ions will be reduced to Cu^+ before they are precipitated using SCN^-.

$$2Cu^{2+} + HSO_3^- + H_2O \rightarrow 2Cu^+ + HSO_4- + 2H^+$$

$$Cu^+ + SCN- \rightarrow CuSCN$$

Solubility of CuSCN increases with pH, so excessive amounts of ammonium ions should be absent., as should also oxidizing agents. The solution should be only slightly acidic, since the solubility of CuSCN increases with decreasing pH because of complexing ability of thiocyanate anions. In this analysis, Pb, Hg, Se, Te and precious metals ions interefere and contaminate the precipitate.

Consequently, the conditions of experiment are as follows:

Slight acidity with respect to HCl or H_2SO_4. The presence of a reducing agent, for instance H_2SO_3 or NH_4HSO_3, to reduce Cu(II) to Cu(I). A slight excess of NH_4SCN. A large excess increases the solubility of the copper thiocyanate due to formation of a complex. The absence of oxidizing agents.

The precipitate is curdy and readily coagulates by boiling. It is washed with dilute ammonium thiocyanate with an addition of H_2SO_3 or NH_4HSO_3, to avoid oxidization of Cu(I).

Chemicals:

1. 5-6% aqueous solution of NH_4HSO_3;
2. Freshly prepared 10% aqueous solution of NH_4SCN.

Procedure:

1. Place the sample solution containing not more than 0.1 g of Cu2+ ions in a beaker á 250 mL. Add water to a total 50 mL, and next few drops of 2M HCl and 25 mL of NH_4HSO_3 solution.
2. Dilute the content of the beaker to 150-200 mL, heat nearly to boiling and add slowly, stirrling constantly with a glass rod, solution of NH_4SCN in slight excess. The precipitate should be white, the mother liquor should be colorless and smell of SO_2.
3. Leave the beaker covered to the next lesson1.
4. (Next lesson) Filter through glass crucible G4, under vacuum2. Wash the precipitate at lest 10 times with cold solution made by adding 1 mL of solution of NH_4SCN and 1 mL of solution of NH_4HSO_3 to 100 mL of water.

5. Dry the crucibles at 110°C, during 90 min or more. Place them in dessicator for a 30 min and weigh using an analytical balance.

Attention:

The glass rods In the beakers (each beaker should have its own rod) must be there all the time, to the end of analysis. Do not remove them even for a moment!

Little amount of the precipitate on beaker's walls difficult to be washed down during filtering does not influence the result too much.

After experiments, do not wash the crucibles – the laboratory staff will do it better. The beakers can be washed easily using a sponge and hot water with a detergent.

Calculations and report The final report should contain masses of empty and full filters, calculated masses of the precipitated CuSCN, calculations made to achieve the final result, and – if necessary – the brief analysis of the results. The result is mass of elemental copper in each sample (in grams) and the averaged weight percent of Cu in the alloy or mineral under examination.. The ratio of molecular masses of Cu to CuSCN is 0.5225.

4E. Gravimetric estimation of Ba(II) as BaSO4

Aim: To estimate the weight of barium present in the whole of the given solution

Objectives

The objectives of this laboratory are as follows:

•To experimentally analyze an unknown sulfate salt via a precipitationreaction, using the techniques associated with Gravimetric Analysis to collectand weigh the precipitate, and

•To calculate the percentage by mass of $SO_4^{-}2$in the unknown sulfate salt via a stoichiometric analysis of the collected precipitate, and then use thispercentage to identify the metal "M" present in the sulfate salt.

Procedure:

The given solution of barium chloride is made upto 100ml in a standard flask with distilled water. 20 ml of made up solution is pipetted out into a clean 400ml beaker provided with a watch glass and a glass rod. The solution is diluted to 50ml with distilled water and acidified with 2ml of dilute hydrochloric acid and heated to boiling. To the hot solution added about 20ml of hot 5N H2SO4 very slowly with constant stirring. The precipitated barium sulphate is digested over a steam bath for half an hour and allowed to settle. Tested for complete precipitation by adding 2 drops of 5N sulphuric acid to the supernatant liquid in the beaker. Then the precipitate is filtered through whatmann No. 41 filter paper using hot water as wash solution. The filter paper along with the precipitate is incinerated in a preheated and weighed silica crucible. It is cooled and weighed. Heating, cooling and weighing are repeated to constant weight. A duplicate is also performed.

Result

The amount of barium present in the whole of the given solution is A = d g ; B = f g

S. No.	**Object to be weighed**	**Weight in grams**	
		Crucible A	**Crucible B**
1	Empty silica crucible		
2	Silica crucible + barium sulphate		
3	Barium sulphate		
	Weight of barium sulphate	**a**	**b**

Calculation

Molecular weight of barium sulphate = 233.40

Atomic weight of barium = 137.34

Crucible A

233.40 g of barium sulphate contains 137.34 g of Ba

a g of barium sulphate contains $\frac{137.34 \times \mathbf{a}}{233.40}$

= **c** g of Ba

20 ml of the given barium solution contains **c** g of Ba

∴ 100 ml of the given barium solution contains $\frac{\mathbf{c} \times 100}{20}$

= **d** g of Ba

Crucible A

233.40 g of barium sulphate contains 137.34 g of Ba

b g of barium sulphate contains $\frac{137.34 \times \mathbf{b}}{233.40}$

= **e** g of Ba

20 ml of the given barium solution contains **e** g of Ba

∴ 100 ml of the given barium solution contains $\frac{\mathbf{e} \times 100}{20}$

= **f** g of Ba

4F. Gravimetric estimation of Pb(II) as $(Pb)_3(PO_4)_2$

Aim

To estimate the weight of lead present in the whole of the given solution.

Procedure

The given solution is made upto 100ml in a standard flask using distilled water. 20 ml of this is pipetted out into a clean 400ml beaker provided with a watch glass and glass rod and is diluted to about 50ml. This solution is heated to boiling and to this hot solution 20 ml of dilute sodium hydrogen phosphate is added in drops with constant stirring and then 40 ml of alcohol. The precipitate is allowed to settle and filtered through Whatman 41 filter paper using 10% dilute alcohol as wash solution. The precipitate is dried. After drying, the precipitate is carefully removed from the filter paper and kept in a safe place. The filter paper alone is then incinerated in a preheated and weighed silica crucible. The crucible is cooled, a drop of concentrated sulphuric acid is added and heated again. It is cooled in a desicator and then weighed along with the precipitate already removed from the filter paper. A duplicate is performed.

Result

The amount of lead present in the whole of the given solution is A = d gm; B = f gm

S. No.	**Object to be weighed**	**Weight in grams**	
		Crucible A	**Crucible B**
1	Empty silica crucible		
2	Silica crucible + lead sulphate		
3	Lead sulphate		
	Weight of lead sulphate	**a**	**b**

Calculation

Molecular weight of lead sulphate = 303.25

Atomic weight of lead = 207.19

Crucible A

303.25 g of lead sulphate contains 207.19 g of lead

a g of lead sulphate contains $\frac{207.19 \times \mathbf{a}}{303.25}$

= **c** g of lead

20 ml of the given lead solution contains **c** g of lead

∴ 100 ml of the given lead solution contains $\frac{\mathbf{c} \times 100}{20}$

= **d** g of lead

Crucible B

303.25 g of lead sulphate contains 207.19 g of lead

b g of lead sulphate contains $\frac{207.19 \times \mathbf{b}}{303.25}$

= **e** g of lead

20 ml of the given lead solution contains **e** g of lead

∴ 100 ml of the given lead solution contains $\frac{\mathbf{e} \times 100}{20}$

= **f** g of lead

5. Analysis of Metals and Alloys

5A. Quantitative estimation of iron in cast iron and steel.

The basis of the metallic iron determination method in this study is the following chemical reaction:

$$Fe + CuSO_4 \longrightarrow FeSO_4 + Cu$$

Solid metallic iron replaces the Cu^{2+} in the solution and becomes Fe^{2+}. Solid metallic iron content can be determined by determining the Fe^{2+} content in the solution. The objective of this study is to develop an accurate method to determine the metallic iron content in the steel-making by-products, whereby this method can also be used for the determination of metallic iron content for direct reduced iron and related materials.

Experimental

Sample Preparation for analytical samples

The test sample shall be repetitively pulverized or ground and screened at 65 mesh to the point where confidence exists that the + 65 fraction is 100% metallic in nature. The -65 mesh portion will be tested in the following procedure.

Experimental

Sample Preparation for analytical samples

The test sample shall be repetitively pulverized or ground and screened at 65 mesh to the point where confidence exists that the + 65 fraction is 100% metallic in nature.

The -65 mesh portion will be tested in the following procedure.

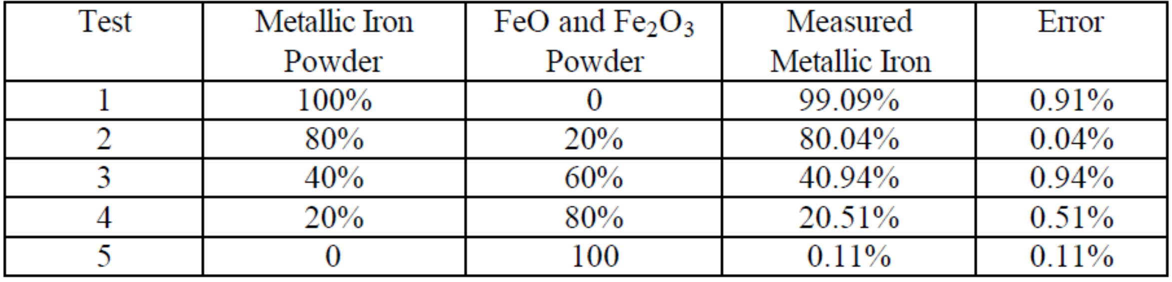
Metallic Iron Determination Procedures

- Weigh 0.5 gram sample and put it into a beaker
- Put 50 ml 0.5M CuSO4 into beaker
- Put 50 ml distilled water into beaker
- Put beaker on hot plate and let boil for 45-60 minutes (covered with watch glass), stir with glass bar in order to prevent powder sample from agglomerating, and add distilled water as necessary to keep solution a constant level in the beaker.
- Filter into 250 ml flask right after boiling, dilute the solution to 200 ml or so with distilled water, and then add HCl to adjust the pH value of the solution to equal or less than 1.
- Add the distilled water to 250 ml
- Determine the metallic iron content by ICP.

Five synthetic samples, mixing the pure metallic iron powder and iron oxide powder (a mixture of FeO and Fe2O3), were tested to verify the test method. Six slag samples from the different sites have also been tested.

Results and Discussion

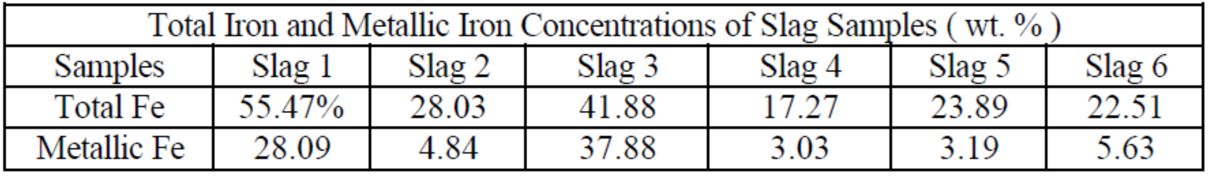
Table 1. Test results for five synthetic samples



Test	Metallic Iron Powder	FeO and Fe_2O_3 Powder	Measured Metallic Iron	Error
1	100%	0	99.09%	0.91%
2	80%	20%	80.04%	0.04%
3	40%	60%	40.94%	0.94%
4	20%	80%	20.51%	0.51%
5	0	100	0.11%	0.11%

The results given in Table 1 demonstrate the overall error for metallic iron analyses is less than 1%.

Table 2. Iron Analyses for six Slag Samples from Different Sites



Total Iron and Metallic Iron Concentrations of Slag Samples (wt. %)						
Samples	Slag 1	Slag 2	Slag 3	Slag 4	Slag 5	Slag 6
Total Fe	55.47%	28.03	41.88	17.27	23.89	22.51
Metallic Fe	28.09	4.84	37.88	3.03	3.19	5.63

The results given in Table 2 indicate different steel slags have different iron units and different metallic iron contents. Accurate measurement of metallic iron content provides a key parameter for reusing and recycling of the steel slag.

The method to analyze the metallic iron in this project is relatively easy.

However, there are several factors to affect accurate test results. The main factors include sample preparation, sample handling, and pH values. First of all, the slag samples have to be ground to pass 65-mesh (-65 mesh) and to liberate the metallic iron out. When the slag particle is too big, the metallic iron may still be covered by the non-metal materials and cannot have contact with Cu2+, which will cause analytical error. It is difficult to grind the metallic iron part of the slag, and some part of metallic irons cannot pass 65-mesh (+65 mesh). Combining the test results of two parts (-65-mesh and + 65-mesh) on a weighted percentage basis will give the total metallic iron for the slag sample.

Continuous stirring of the testing solution is also very important for obtaining accurate results, because no stirring will lead the Cu precipitates to form a Cu thin film around the metallic iron particles and prevent Cu2+ from further attacking the inside of the metallic iron particle.

The pH value of the testing solution is another key factor for the metallic iron analysis. When boiling the slag sample in 0.5 M CuSO4 solution, the pH value should be around 7. If the CuSO4 solution pH value is too high, the iron oxide will partially dissolve into the solution, which will interfere with the metallic iron concentration and exaggerate the metallic iron content in the slag.

After boiling the slag sample, the solution should be filtered immediately. When the solution temperature begins to decrease, the Fe2+ and Fe3+ will partially precipitate to form Fe(OH)2 and Fe(OH)3, especially for the high metallic iron content slag. The pH value of the filtrate should be adjusted to 1 in order to avoid the precipitation of Fe(OH)2 and Fe(OH)3. When the concentration of iron in the filtrate is high, a brown precipitate is observed from the solution right after filtering if no adjusting of the pH value takes place.

The pH value and temperature determine the solubility of Fe(OH)2 and Fe(OH)3.

One factor that needs to be considered is the oxidation of Fe2+ to Fe3+ in water. If oxygen is present, some of the Fe(II) oxidizes to Fe(III).

$$Fe^{2+} + H^{+} + 0.25O_2 = Fe^{3+} + 0.5H_2O.$$

The time for complete oxidation of Fe2+ is a matter of minutes in an aerated solution when pH is above 7.0.

The following are the solubility equilibriums of Fe(OH)2 and Fe(OH)3, respectively:

Fe(OH)2 (s) = Fe2+(aq) + 2OH-(aq), Ksp = [Fe2+][OH-]2= 4.87 x 10-17 , and

Fe(OH)3 (s) = Fe3+ (aq) + 3OH- (aq), Ksp = [Fe3+][OH-]3 = 2.79 x 10-39

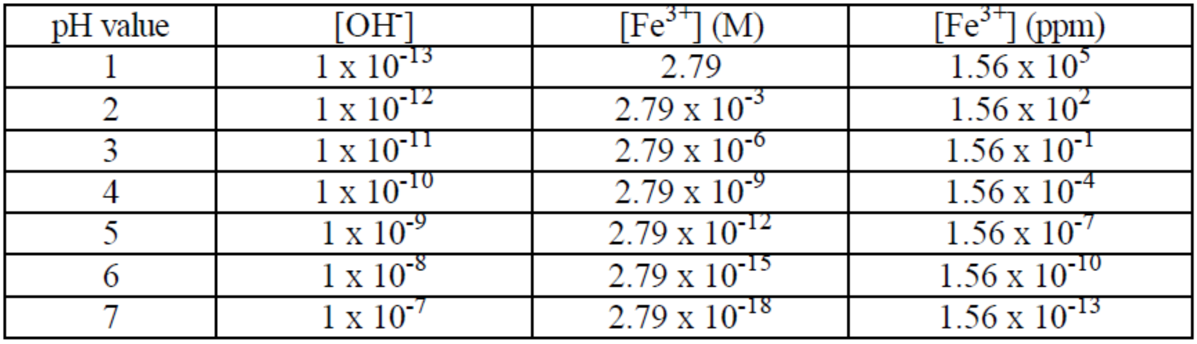
Ksp is the solubility product constant

Because the Ksp for Fe(OH)3 is much smaller than that of Fe(OH)2, it is only necessary to find the maximum pH value of the filtrate to prevent Fe(OH)3 from forming a precipitate. Since Ksp is so small, the [OH-] from the Fe(OH)3 dissolution is negligible compared to the [OH-] from the dissociation of water. Ksp = [Fe3+][OH-]3 = 2.79 x 10-39 [Fe3+] = 2.79 x 10-39 / [OH-]3

In order to prevent precipitate generation for different Fe3+ concentrations, the required maximum pH values are given in Table 3. For example, when pH = 2, the maximum Fe3+ concentration is 156 ppm:

[Fe3+] = (2.79 x 10-3M) (55.845 g/mol) = 0.156 g/L = 1.56 x 102 ppm(μg/ml)

Table 3. The maximum pH values needed for the different Fe^{3+} concentrations.



pH value	$[OH^{-}]$	$[Fe^{3+}]$ (M)	$[Fe^{3+}]$ (ppm)
1	1×10^{-13}	2.79	1.56×10^{5}
2	1×10^{-12}	2.79×10^{-3}	1.56×10^{2}
3	1×10^{-11}	2.79×10^{-6}	1.56×10^{-1}
4	1×10^{-10}	2.79×10^{-9}	1.56×10^{-4}
5	1×10^{-9}	2.79×10^{-12}	1.56×10^{-7}
6	1×10^{-8}	2.79×10^{-15}	1.56×10^{-10}
7	1×10^{-7}	2.79×10^{-18}	1.56×10^{-13}

Usually, the concentration of 0.5 gram pure metallic iron (100% iron) in the 250 ml solution is 2000 ppm. So, the pH value for the test solution should be less than 2.

Quantitative estimation of Zn(II) and Cu(II) in brass sample by volumetry

Direct analysis of zinc content by EDTA complexometry.

This method was originally developed for analysis of mineral samples and was adapted for application to plating bath analyses. Similar to many others found in literature, the method involves cyanide decomposition with an oxidant, to release copper and zinc ions. In this titration, xylenol orange is used as an indicator at a pH ranging from 5.0 to 5.5 (stabilized by an acetate buffer solution). This metal indicator is not specific for zinc, as it also binds to copper. Thus, during the titration it is necessary to use a masking solution. One of the great advantages of this method is the elimination of formaldehyde in the analysis, which as already mentioned is a potential carcinogenic agent and creates problems if too little or too much is used.

Formaldehyde is replaced by a masking solution based on sodium thiosulfate which acts to reduce Cu(II) to Cu(I). In the univalent state, copper does not bind with EDTA. The following reaction shows the reduction of Cu(II) by thiosulfate.

$$2Cu^{+2} + 2S_2O_3^{-2} \rightarrow 2Cu^{+} + S_4O_6^{\ -2}$$

The titration endpoint is noted by the color change from purple to yellow. The proposed methodology is as follows:

(a) Pipette an aliquot of plating solution into a 250 mL Erlenmeyer flask. The aliquot volume will depend on the actual concentration of zinc ions in the brass plating bath. The following volumes are recommended:

- 2 mL for zinc contents above 20 g/L
- 5 mL for zinc contents from 10 g/L to 20 g/L
- 10 mL for zinc contents from 5 g/L to 10 g/L
- 20 mL for zinc contents below 5 g/L.

(b) In a fume hood, add ammonium persulfate crystals [$(NH_4)_2S_2O_8$] until the solution turns to a dark green color. This process is exothermic. The purpose of this step is cyanide decomposition. During this step the solution can turn to a brown color before turning green. If the brown color persists, interrupt the analysis and begin the procedure again. As an alternative to persulfate, concentrated nitric acid (HNO_3) can be used, followed by the addition of concentrated sulfuric acid (H_2SO_4) and heating until white or brown fumes disappear.

(c) Add 10 mL of distilled water and let it cool.

(d) Add acetate buffer solution (pH 5.5) to bring the pH value to around 5.5. After that, the solution turns blue, characteristic of Cu(II) ions in aqueous solution. The composition of this buffer solution is: 150 g of anhydrous sodium acetate ($NaCH_3COO$) and 15 mL of glacial acetic acid for each liter of distilled water.

(e) Add the masking solution until the solution turns to a transparent pale yellow (almost colorless). The amount of masking solution added will depend on the copper content in the brass bath. Usually, 20 to 50 mL is necessary. The composition of this masking solution is: 100 g of sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) for each liter of distilled water.

(f) Add about 0.1 g of 0.1% xylenol orange indicator (m/m). In this step, the solution turns purple. The indicator is prepared as follows: 1 part of indicator ground with 100 parts of NaCl (sodium chloride). The mixture is stored in an amber flask.

(g) Titrate with 0.0575 mol/L standard EDTA solution. The endpoint is easily noticed when the solution turns yellow.

(h) The zinc content in the bath is determined by the following formulas:

$g/L\ Zn = (mL_{EDTA} \times M_{EDTA} \times 65.39)/V_{aliquot}$, or

$g/L\ Zn = (mL_{EDTA} \times cf \times 3.76) / V_{aliquot}$

where:

mL_{EDTA} = volume of EDTA solution in the titration (mL),

M_{EDTA} = molarity of EDTA solution (mol/L),

cf = correction factor for the 0.0575 mol/L EDTA solution.

$V_{aliquot}$ = aliquot solution volume (mL).

Direct analysis of copper content by iodometric titration

This method is quite practical and suitable for the direct determination of copper content in brass solutions because there is no zinc interference, as already mentioned.

The proposed methodology is as follows:

(a) Pipette 2 mL of the plating solution into a 250 mL Erlenmeyer flask.

(b) In a fume hood, add 15 mL of concentrated nitric acid and 5 mL of concentrated sulfuric acid. The purpose of this step is cyanide decomposition as well as oxidation of Cu(I) to Cu(II). In this procedure, ammonium persulfate cannot be used because the excess of this salt cannot be eliminated efficiently. This causes significant analytical errors.

(c) Heat the flask solution (at the fume hood) until the solution turns blue-green and the white or brown fumes disappear. After that, add 20 mL of distilled water and let it cool. The purpose of this step is to eliminate the excess nitric acid.
(d) Add 5 g of potassium iodide (KI). The flask solution will turn brown.
(e) Titrate with a solution of fresh pre-standardized 0.1 N sodium thiosulphate pentahydrate (Na2S2O3·5H2O) until the solution color turns pale yellow.
(f) Add 0.5 mL of a fresh 1% starch indicator solution (The solution turns dark blue.) and continue the titration until the dark color disappears.
(g) The copper content in the bath is determined by the following
formulas:
g/L Cu = mLthiosulfate × Nthiosulfate × 31.785, or
g/L Cu = mLthiosulfate × cf × 3.1785
where:
mLthiosulfate = volume of sodium thiosulfate consumed in the titration (mL),
Nthiosulfate = normality of sodium thiosulfate solution (N),
cf = correction factor for the 0.1 N sodium thiosulfate solution.

5B. Quantitative estimation of manganese in pyrolusite

Aim: Estimation of manganese in pyrolusite.

Theory: Pyrolusite ore contains a large amount of manganese in the form of manganese dioxide, MnO_2, and little silica. It is a black mineral. Its manganese content is between 60 to 63 % and silica content is between l0 to l5% .The dissolution of the ore is done in the mixture of conc. HCl and conc. HNO_3. The insoluble residue contains silica (SiO2) and soluble part contains largely manganese. Manganese is estimated volumetrically, using KMnO4. Potassium permanganate is a powerful oxidizingagent in acidic medium and hence can be usedto estimate Mn volumetrically. Themethod is called Volhard's method.

Chemicals: conc. HCl, conc. HNO_3, conc. H_2SO_4, Zinc oxide paste (emulsion), KMnO4solution (approx. 0.1 N) oxalicacid

Apparatus: Stem-cut funnel, Silica crucible, 100 ml. Volumetric flask

Procedure: **Dissolution of the ore:**

1. Weigh accuratelyabout 0.3 to 0.4 g of the ore. Call it as w g. Transfer it in aconical flask.
2. Add to it l0 ml. conc. HCl and 3 ml. conc. HNO_3. Cover it with a stem-cut funnel which actsas an air condenser.
3. Heat the flask in a fuming cupboard on a low flame till black particles of the ore dissolve. If the ore does not dissolve, again add 2 ml. conc. HCI and 1 ml. conc. HNO_3 and heat it again.
4. Repeat theprocedure till the ore dissolves.
5. Cool the flask and add 2 ml. conc. H2SO4slowly from the sides of flask.
6. Heat the flask again till white copious fumes of SO3start evolving.
7. Cool the solution and rinse the funnel and its stem with little distilled water in the same flask.Add to it about 20 ml. distilled water.

Estimation of silica (SiO_2) gravimetrically:

1. Filter the above solution through whatman No. 41 filter paper collect the filtrate in a 50ml.beaker. Transfer all the silica in a filter paper. Wash it with hot water till the residueis Free from chloride (test with $AgNO_3$) and acid (test by blue litmus paper). Collec the filtrate

and was hings in the same beaker. Dilute it to exactly 100 ml in a volumetric flask. Preserve it for the volumetric estimation of Mn.

2. Dry the filter paper on a metal cone at 110 to 1200C.

3. Ignite the residue along with the filter paper in previously weighed silica crucible and heat it for about 30 - 40 minutes. Cool the crucible and its lid.

4. Weigh the crucible with lid and the residue. Find the weight of SiO_2. Call as X g. Calculate the percentage of SiO_2 in the ore. Repeat this operation till constant weight.

Estimation of Mnyolumetrically (Volhards method) Principle: This method is based on the oxidation of divalent manganese with potassium permanganate in a hot (not less than 80°C) solution neutralised with zinc oxide and containing a little excess of the latter. The endpoint is indicated by the persistent pink colour. Solid zinc oxide have a tendency to adsorb manganese ion.Potassium permanganate was stable in boiling hot solution at pH 7.08 which was obtained by saturation with zinc oxide. Fading in pink of potassium permanganate observed near the end point of the titration During the dissolution of pyrorusite ore, MnO_2 gets converted to $MnSO_4$ i,e, Mn (IV) gets converted to Mn (II). Volhard,s method is based on the principle that when manganoussalt solution is warmed and titrated with standard $KMnO_4$ solution turns to brown and dark precipitate of hydrated manganesedioxide is obtained. During the reaction manganous ion isoxidizedand permanganate ion is reduced giving hydrous manganese dioxide.

2KMnO4+ 3MnSO4+ 2H2O ⟶ K2SO4+ 5MnO2+2H2SO4

i.e. 3Mn2++ 2MnO4-+ 2H2O ⟶ 5MnO2+ 4H+

Hydrated manganese dioxide has acidic properties and absorbs manganous hydroxide Preventing complete oxidation. This difficulty is avoided by introducing sufficient amount ofZnO paste.FunctionofZnOpaste(emulsion):i) The precipitate hydrated of MnO2 settles very quickly.

ii) It neutralisesH2SO4which is added during the titration of manganese

iii) It avoids formation of potassium permanganate.

iv) It avoids formation of manganous acid, hence prevents precipitation of manganous manganite.

v) It forms Zn ferrite with Fe if present as an impurity in MnSO4. Thus interference of Fe is masked.

Reactions:

MnO2+ 4HC1 ⟶ MnC12+ 2H2O + Cl2

MnO2+ 4HNO3 ⟶ Mn(NO3)2+ 2H2O + 2NO2+O2

MnCl2+ H2SO4MnSO4+ 2HC1 ⟶ Mn(NO3)2+ H2SO4MnSO4+ 2HNO3

2KMnO4+ **3MnSO4**+ 2H2O ⟶ **5MnO2**+ K2SO4+2H2SO4

ZnO + H2SO4 ⟶ ZnSO4+ H2O

Procedure: Part I -Preparation of standard 0.1N Oxalic acid solution (Eq. Wt.63)

1000 ml 1N oxalic acid solution contains 63 g of oxalic acid.1000 ml 0.1N oxalic acid solution contain 6.3 g of oxalic acid.

250ml 0.1N oxalic acid solution contain 1.575 g of oxalic acid.

Weigh accurately 1.575 g of oxalic acid ($H_2C_2O_4.2H_2O$) on a watch glass. Transfer it in a beaker and rinse the watch glass with little water in the same beaker. Dissolve it in about 50ml distilled water. Transfer it into 250 ml volumetric flask. Dilute it up to the mark using distilled water. Use of this solution for standardization $KMnO_4$solution.

Part II :Standardisation of $KMnO_4$solution :

1. Fill burette no.1 by 0.1 N (approx.)$KMnO_4$ solution.Fill burette no.2 by 0.1 N oxalic acidTake by burette no.2, 10ml of 0.1 N oxalic acid and add to it 15 ml 2N H_2SO_4solution
2. Heat the solution on wire gauze to 70oC and titrate this hot solution with $KMnO_4$solutionadded from burette no.1.
3. The end point of the titration is noted when permanent faint pink colourappears. Call this
4. burette reading as X1ml.
5. To the same solution, add one ml oxalic acid solution by burette no.2 and heat the flask to
6. 70oC.The solution becomes colorless.
7. To this hot solution, add $KMnO_4$solution from burette no.1 till faint pink colour appears.
8. Call this burette reading as X2ml.
9. To the same solution, add one ml oxalic acid solution by burette no. 2 and heat the flask to70oC.The solution becomes colorless.
10. To this hot solution, add $KMnO_4$solution from burette no.1 till faint pink colour appears.
11. Call this burette reading as X3ml.
12. From these three burette readings find out the exact normality of $KMnO_4$solution.

Part III : Estimation of Manganese :

1. Fill the burette no.1 by standardized $KMnO_4$solution.and burette no.2 with diluted solution

of $MnSO_4$.

2. Take by burette no.2, 10 mlof the diluted solution of $MnSO_4$. Add 1/2 test tube of ZnOpaste.
3. Add one test tube water to it.
4. Heat the solution on water bath between 40 and 600C and add 2 to 3 drops of 2N HNO_3solution(which promotes the settling of the ppt. of MnO_2at the bottom).
5. Titrate this hot solution with standardised $KMnO_4$solution from burette no.1 with constant

shaking.The end point is faint pink colour to supernatant liquid which persists even after vigorousshaking. Note down this burette reading .The faint pink colour should remain as it iseven after heating, if not add one or two drops of $KMnO_4$solution.

6. Take two more readings. Find the constant burette readingas Y ml.

Standardisation of $KMnO_4$solution –Burette 1	:	0.1 N (approx) $KMnO_4$solution
Burette 2	:	0.1 N exart $H_2C_2O_4$. $2H_2O$ solution
Indicator	:	$KMnO_4$ act as a self indicator
End Point	:	Colourless to pink

Burette –2	10 ml	12ml	14ml
Burette –1	X_1=ml	X_2= ml	X_3= ml

Calculations:-

Find out exact normality of $KMnO_4$

$KMnO_4$ = Oxalic acid

$N_1 x X_1 = 0.1 x 10$ $\therefore N_1 = \frac{0.1x10}{X_1}$

$N_2 x X_2 = 0.1 x 12$ $\therefore N_2 = \frac{0.1x12}{X_2}$

$N_3 x X_3 = 0.1 x 14$ $\therefore N_3 = \frac{0.1x14}{X_3}$

Exact normality of $KMnO_4$= mean N_4 $= \frac{N_1 + N_2 + N_3}{3}$

Estimation of Mn from a given solution –

Observation and Observation Table –

Burette 1 : 0.1 N (approx) $KMnO_4$ solution
Burette 2 : diluted Mn^{2+} solution
Indicator : $KMnO_4$ act as a self indicator
End Point : Colourless to pink

Burette – 2	10 ml	10 ml	10 ml	C.B.R
Burette – 1	Y_1 = ml	Y_2 = ml	Y_3 = ml	Y= __ ml

Estimation of Manganese: (Volumetrically)

1000 ml 1 N $KMnO_4$ = 16.462 g of Mn.

Y ml N_4 Normal $KMnO_4$ = ? $\therefore \frac{YxN_4 x16.46}{1000}$ = Z g of Mn

10 ml dil. solution = Z g of Mn.
∴ 100 ml dil. solution = ?

∴ $\frac{Zx100}{10}$

= A g of Mn
W g of ore = A g of Mn
∴100 g of ore = ? ∴ $\frac{Ax100}{W}$

∴ % of Mn = ---- %

CEM 196: FOOD PROCESSING, PRESERVATION & PACKAGING LAB

I. Preparation of Jams, jellies, syrups, squashes

1. Preparation of Apple Jam:

Theory: Jam is a product made by boiling fruit pulp with sufficient amount of sugar to a reasonably thick consistency, firm enough to hold the fruit tissues in position. Apple, pear, sapota (chiku), peach, papaya, karonda, carrot, plum, straw-berry, raspberry, mango, tomato, grapes and muskmelon are used for preparation of jams. It can be prepared from one kind of fruit or from two or more kinds.

Ingredients:

Apple : 1 Kg
Water : 700 mL
Sugar : 750 gm
Butter: 50 gm
Kaju: 100 gm
Pectin: 10 gm
Citric acid: 5 gm
Sodium benzoate: 1.5 gm

Procedure:

a. Cut all the apples into 4 pieces and take in a pressure cooker.
b. Add 700 mL of water and heat for 3 to whistle.
c. Strain the cream and heat with sugar and butter.
d. Add kaju.
e. When it becme thick, add pectin (10 gm, mixed with sugar).
d. Add sodium benzoate.

e. Check the thickening and pour into bottle and then seal after some time.

Yield: Measure the weight

2. Preparation of Papaya Jelly

Theory: A jelly is a semi-solid product prepared by boiling a clear, strained solution of pectin-containing fruit extract, free from pulp, after the addition of sugar and acid. A perfect jelly should be transparent, well-set, but not too stiff, and should have the original flavour of the fruit. It should be of attractive colour and keep its shape when removed from the mould. It should be firm enough to retain a sharp edge but tender enough to quiver when pressed. Guava, sour apple, plum, karonda, wood apple, loquat, papaya and goose-berry are generally used for preparation of jelly. Apricot, pineapple, strawberry, raspberry, etc. can be used but only after addition of pectin powder, because these fruits have low pectin content.

Ingredients:

Papaya: 1 kg
Water: 700 mL
Sugar : 750 gm
Butter : 50 gm
Pectin : 10 gm
Citric acid : 5 gm
Coloring agent : 2 to 3 drops

Procedure:

a. Cut all the papaya into small pieces and take in a pressure cooker.
b. Add 700 mL of water and heat for 3 to 4 whistle.
c. Add citric acid (2 gm) during boiling.
d. Strain the extract.
e. Add Pectin (mixed with sugar) and then boil again.
f. Judge the end point by drop test.
g. Remove the scum or foam.
f. Add the coloring agent and the remaining citric acid.
g. Fill into hot, clean sterilized bottles, capped them and sealed them after some time.

Yield: Measure the weight

3. Preparation of Orange Syrup

Theory: This type of fruit beverage contains 25% fruit juice (or) pulp, 65% TSS, 1.3 to 1.5% acidity and 350 ppm of SO_2 or 600 ppm of KMS. It is diluted before serving, Fruits like aonla, jamun, pomegrante, grape, lemon, orange and sometimes ginger can be used for the preparation of syrup. It is also prepared from extracts of rose, sandal almond etc.

Heavy sugar syrup of 70-75 % strength is used as the base of all synthetic syrups and they are flavoured and coloured with artificial essence/flavours and colours. They never contain fruit pulp/juice. A large proportion of these syrups can, however, be replaced by real fruit juices, squashes and syrups which are more nutritious.

Large quantities of synthetic syrups (orange, lemon, pineapple, strawberry) are manufactured and sold in various countries. These can be prepared by using 1.5 kg of sugar, 500 ml of H_2O and 15 g of citric acid. Different colours and flavours are added as required. Among colours, orange red, lemon yellow, green, raspberry red etc. are mostly used, while artificial essence/flavours of rose, orange, pineapple, strawberry, lemon etc. are added as flavouring substances.

Ingredients:

- Granulated sugar- 750 gm
- Water – 750 mL
- Oranges – 1 Kg
- Citric acid – 2 gm

Procedure:

- Remove the peel of all the oranges, try to remove only the orange part without the pith.
- Place the peel in a saucepan, pour in enough water to cover the peel.
- Bring it to boil and strain (this will help to get rid of the bitter taste).
- Cut the fruit and extract the juice
- Dump the peels into a saucepan, add 500 g sugar and 500 mL water, bring it to boil and gently simmer for 20 minutes. Then pour in the orange juice and keep on simmering for 8-10 minutes.
- Add citric acid and mix.
- Cover with a lid and let it sit in a cold place for 24 hours.

- Strain the Juice.
- Pour into a glass jar and seal tightly with a lid.

Yield: Measure the final volume

4. Preparation of Squash:

Theory: This is a type of fruit beverage containing atleast 25% fruit juice (or) pulp, 45% TSS, 1.0% acidity and 350 ppm of SO_2 (or) 600 ppm of sodium benzoate. It is diluted before serving. Lime, mango, orange and pineapple are used for making squash commercially using KMS as preservative or fruits viz. jamun, passion fruit, raspberry, strawberry, grape fruit etc. with sodium benzoate as preservative.

Ingredients:

Lemon: 25 – 30 pcs
Sugar : 750 gm
Water : 750 mL
KMS
Citric acid: 1 gm
Colouring agent

Procedure:

a. All the lemons are squeezed using a squeezer and it is filtered.
b. Sugar syrup is prepared by boiling 750 gm of sugar with 750 mL of water.
c. Then it is filtered with a clean cloth to remove dirt and then cooled.
d. The sugar syrup and the lemon syrup are mixed.
e. KMS is added.
f. Finally the mixture is poured in cleaned bottles and packed.

Yield: Measure the final volume

II. Preparation of mixed fruit Juice:

Theory: All fruits are not suitable because of difficulties in extracting the juice or because the juice is of poor quality. The variety and maturity of the fruit and locality of cultivation influence the flavour and keeping quality of its juice. Only fully ripe fruits are selected. Over ripe and green fruits, if used, adversely affect the quality of the juice.

Ingredients

Aloe vera gel : 2 table spoon
Oranges : 1 Kg
Apple : 750 gm
Black grapes : 500 gm
Banana : 500 gm
Sugar : 750 gm
Sodium carboxy methyl cellulose (CMC) : 1 gm
Citric acid : 5 gm
Sodium Benzoate : 1.5 gm
Vitamin E oil : 1 drop

Procedure:

a. Wash the aloe vera leaf under running water to remove the yellowish liquid known as ‘latex’ and any dart particle and then pat it dry with the help of a clean cloth.
b. Use a sharp knife to cut the side rind off the leaf and pull it apart.
c. Peel the yellow layer just beneath the rind with a sharp knife.
d. Use a spoon to gather all the clear aloe vera gel.
e. Wash and rinse all the fruits and remove tough and bitter parts from them. Also remove their seeds and stems.
f. Chop the fruits into the appropriate-sized chunks, pieces or slices.
g. Use seedless grapes, and make sure there are no stems lingering. Peel oranges and take out its slices. Peel the apples and cut into thin slices or pieces. Peel bananas and cut into thin slices.
h. Prepare the juicer by cleaning and sanitizing before use.
i. Put the pieces of apple, oranges, grapes and banana in the mixer and blend for 2 minutes.
j. Add sugar and blend for one more minute.
k. Add CMC followed by citric acid and sodium benzoate and blend for 30 seconds.
l. Take out the juice from the blender into the strainer and discard the rough particles of it.
m. Add vitamin E oil.
n. Fill the glass bottles and then seal after some time.

Yield: Measure the final volume

III. Estimation of food value:

1. Determination of Total protein of a food sample:

Objective:

To find out the amount of crude protein in a given food sample.

Introduction:

The protein content of foods can be determined by numerous methods. The Kjeldahl, nitrogen combustion (Dumas) and infrared spectroscopy methods for protein analysis are based on nitrogen determination. The methods are from the Official Methods of Analysis of AOAC International, and are used commonly in research laboratories working on proteins.

Theory:

Nitrogen is one of the five major elements found in organic materials such as protein. This fact was recognized by a Danish chemist, Johan Kjeldahl, who used it as a method of determining the amount of protein in samples taken from a wide variety of organisms. In 1883 Kjeldahl presented to the Danish Chemical Society a method (much revised since his day) for determining the amount of nitrogen in mixtures of substances containing ammonium salts, nitrate, or organic nitrogen compounds.

The central basis used in this procedure is the oxidation of the organic compound using strong sulfuric acid. As the organic material is oxidized the carbon it contains is converted to carbon dioxide and the hydrogen is converted into water. The nitrogen, from the amine groups found in the peptide bonds of the polypeptide chains, is converted to ammonium ion, which dissolves in the oxidizing solution, and can later be converted to ammonia gas.

The Kjeldahl method of nitrogen analysis is the worldwide standard for calculating the protein content in a wide variety of materials ranging from human and animal food, fertilizer, waste water and fossil fuels.

Principle:

The Kjeldahl procedure can be basically divided into three parts: (1) digestion, (2) distillation, (3) titration. In the digestion step, organic nitrogen is converted to an ammonium in the presence of a catalyst at approximately 370ºC. In this experiment, the sample is digested in H_2SO_4, using Copper-based catalyst, converting N to NH_3 which is distilled and titrated.

$$\text{Protein} \xrightarrow[\text{Heat, catalyst}]{\text{Sulfuric acid}} (NH_4)_2SO_4$$

In the distillation step the digested sample is made alkaline with NaOH and the nitrogen is distilled off as NH_3. This NH_3 is trapped in a boric acid solution.

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + Na_2SO_4 + 2H_2O$$

$$NH_3 + H_3BO_3 \text{ (boric acid)} \longrightarrow NH_4 + \underset{\text{(borate ion)}}{H_2BO_3^-}$$

The amount of ammonia nitrogen in this solution is quantified by titration with a standard HCl solution. A reagent blank is carried through the analysis and the volume of HCl titrant required for this blank is subtracted from each determination.

$$H_2BO_3^- + H^+ \longrightarrow H_3BO_3$$

This analysis determines total nitrogen and not usable nitrogen and this is the reason it is called a crude protein analysis.

Procedure:

a. A finely ground 0.8 gm of food sample powder was transferred to a digestion tube.
b. Add 0.5 gm of digestion mixture and 12 mL of concentrated H_2SO_4.
c. The sample was digested in a digestion unit till it becomes colourless.
d. Then the digestion tubes were cooled and transferred to the distillation unit.
e. 30 mL of 40 % NaOH solution was allowed into the tube.
f. Liberated ammonia gas was absorbed in 4 % boric acid solution containing mixed indicator.
g. The pink colour of the boric acid solution was turned into green and this was titrated against 0.01 N HCl until the pink colour was obtained.
h. The crude protein in percent was obtained by using the following formula:

Protein (%) = [TV × 0.014 × 100 (ml) × 0.01 × 100 × 6.25]/[weight of the sample (gm)×Aliquot used for distillation (ml)]

Where, TV = Titre value

2. Determination of Total carbohydrate of a food sample:

Theory:

Carbohydrates are the important components of storage and structural materials in the plants. They exist as free sugars and polysaccharides. The basic units of carbohydrates are the monosaccharides which cannot be split by hydrolysis into more simpler sugars. The carbohydrate content can be measured by hydrolyzing the polysaccharides into simples sugars by acid hydrolysis and estimating the resultant monosaccharides.

Principle:

Carbohydrates are first hydrolysed into simple sugars using dilute hydrochloric acid. In hot acidic medium glucose is dehydrated to hydroxymethyl furfural. This compound forms with anthrone a gree colored product with an absorption maximum at 630nm.

Materials:

2.5 N-HCl

Anthrone Reagent: Dissolve 200mg anthrone in 100mL of ice cold 95% H2SO4. Prepare fresh before use.

Standard Glucose: Stock – Dissolve 100mg in 100mL water. Working standard – 10mL of stock diluted to 100mL with distilled water. Store refrigerated after adding a few drops of toluene.

Procedure:

1. Weigh 100mg of the sample into a boiling tube.
2. Hydrolyse by keeping it in boiling water bath for 3 hours with 5mL of 2.5 N-HCl and cool to room temperature.
3. Neutralise it with solid sodium carbonate until the effervescence ceases.
4. Make up the volume to 100mL and centrifuge.
5. Collect the supernatant and take 0.5 and 1mL aliquots for analysis.
6. Prepare the standards by taking 0, 0.2, 0.4, 0.6, 0.8 and 1mL of the working standard. ‘0’ serves as blank.
7. Make up the volume to 1mL in all the tubes including the sample tubes by adding distilled water.
8. Then add 4mL of anthrone reagent.
9. Heat for eight minutes in a boiling water bath.
10. Cool rapidly and read the green to dark green color at 630nm.
11. Draw a standard graph by plotting concentration of the standard on the X-axis versus absorbance on the Y-axis.
12. From the graph calculate the amount of carbohydrate present in the sample tube.

Calculation:

Amount of carbohydrate present in 100mg of the sample = [mg of glucose/volume of test sample] × 100

3. Determination of total fat of a food sample:

Principle:

A **Soxhlet extractor** is a piece of laboratory apparatus invented in 1879 by Franz von Soxhlet. It is a procedure to remove lipids (fats) from food. A solvent is used to wash the solid using a reflux apparatus. The sample is dried and ground and placed in a tube above the extraction solvent. When heated, the solvent evaporates into a gas, then cools into a liquid in a condenser. It then leaks into the sample tube. This continues several hours until the lipid is removed from the sample. The solvent is evaporated off, and the amount of lipid is determined.

Reagents and Materials

Ethyl alcohol, 95%
Boiling chips.
Glass wool.
Buchner funnel.
Desiccator.

Procedure:

1. Dry the Soxhlet extraction thimble at 105°C to constant weight. Remove, cool to room temperature in a desiccator, and weigh to the nearest 0.1 mg.

2. Carefully add the sample to the extraction thimble. Do not overfill the thimble, leave at least a 1 cm gap between the sample and the top of the thimble. Weigh the filled thimble to the nearest 0.1 mg. Place a plug of glass wool on top of the sample to prevent sample loss during the extraction.

3. Place several boiling chips into a clean, dry receiving flask or beaker. Weigh the container, with chips, to the nearest 0.1 mg and record as the tare weight of the container.

4. For a conventional Soxhlet extraction:

4.1. Assemble the Soxhlet apparatus using at least 160 mL of 95% ethanol. Insert the thimble and heat at reflux for 24 hours. Periodically check the reflux rate and adjust the heating rate to give four tofive solvent exchanges per hour in the Soxhlet thimble. Approximately 100-120 solvent exchanges are required during the 24 hour period.

4.2. When the extraction time is complete, remove the thimble and carefully transfer the sample to a Buchner funnel. Remove any residual solvent by vacuum filtration and wash the sample thoroughly with 95% ethanol, collecting all of the filtrate. Allow the biomass to air dry in the Buchner funnel while it is still attached to the vacuum system.

4.3. Combine the filtrate from the previous step and any solvent from the upper section of the Soxhlet apparatus with the solvent in the 250 mL flask. Place the flask on the rotary evaporator and remove the solvent under vacuum. Use a water bath temperature of 45 ± 5°C to heat the flask during evaporation.

4.4. After all of the visible solvent is removed by the rotary evaporator, place the flask in a vacuum oven (75-100 torr) at 40 ± 1°C for 24 ± 1 hour. Remove the flask at this time and allow to cool to room temperature in a desiccator. Weigh the flask and record this total weight to the nearest 0.1 mg.

Calculations:

1. Calculate the oven dry weight of the sample, using the average total solids content.

$$\%\ Extractives = \frac{Weight\ container\ plus\ residue - Tare\ wt.\ container}{ODW}\ x\ 100$$

2. Calculate the amount of extractives in the sample, on a percent dry weight basis.

$$ODW = \frac{(Weight,\ thimble\ plus\ sample - Weight,\ thimble)\ x\ \%\ Total\ solids}{100}$$

IV. Preservation of processed food:

Food preservation may be defined as the set of treatment processes that are performed to prolong the life of foods and at the same time retain the features that determine their quality, like color, texture, flavor and especially nutritional value. Food preservation processes have different time scales, ranging from short periods needed for home cooking and cold storage methods, to much longer periods of time required by strictly controlled industrial procedures such as canning, freezing and dehydration.

There are many techniques used to preserve food such as legal food additives, varying levels of food ingredients or components, and new technology. Legal food additives, among other functions, can prevent oxidation and inhibit or destroy harmful microorganisms (molds and bacteria). Vitamin E or vitamin C can serve as an antioxidant in many food products, and benzoate in beverages can act as an anti-microbial agent. We can preserve food by manipulating the levels of food ingredients or components to inhibit the growth of microorganisms or destroy them. For example, keep the food low in moisture content (low water activity), high in sugar or salt content, or at a low pH (less than pH 5).

The preservation of fruits and vegetables entails the partial utilization of the raw material. In some cases, during the process it becomes necessary to add a packing medium, e.g., syrup or brine, while in others the raw material is used alone, as in frozen products. The raw material may be processed differently, depending upon the product to be obtained, e.g. vegetables in sauce, jellies, pickles and juices, for instance. The same raw material may be processed in different ways, as a result of which different products will be manufactured. In general terms, some processing methods are mentioned as below.

- Refrigeration
- Cold storage with modified atmosphere
- Superficial chemical treatments
- Special storage condition
- Packaging systems involving modifications in atmosphere
- Canning
- Freezing
- Dehydration
- Preservation Methods by Chemical Action

Acids, salts and sugars are the principal food preservatives of a chemical nature. Sodium chloride is perhaps the oldest compound serving as a preservative. Acids, mainly lactic, but occasionally including propionic, are produced. Acetic acid in the form of vinegar is used in the manufacture of several pickled products. Benzoic acid, sodium salts - sodium propionate, di acetate and sulfur dioxide, and sodium chloride are added to foods to prevent spoilage. Sugars are employed in the manufacture of jelly, jams, preserves, sweetened condensed milk, sweet pickles, and other products aiding the preservation of the products into which they are incorporated.

Preservation by the addition of sugar: Sugar is generally added in the processing of jams, jellies and sweet. The fruit must be boiled, after which the sugar is added in variable amounts, depending upon the kind of fruit and the product being prepared. The mixture must then continue to boil until it reaches a high level of soluble solids, which allows for its preservation. The addition of sugar combines with certain fruit substances to produce a gel - like consistency, which characterizes the texture of jams and jellies. To achieve this, appropriate acidity levels and sugar content, together with pectin, form a proper gel.

Benzoic acid and benzoate: Benzoic acid is a stable, white, granular or crystalline powder possessing a sweet, stringent taste. The sodium salt is more soluble in water (62.5 g in 100 ml) at 25° C than benzoic acid. For this reason it is the preferred form for industrial use. Sodium benzoate has an optimum pH range between 2.5 and 4.0. If the pH of the food product is above pH 4.5, acidification may be desirable; the benzoate can be 100 times more active at this optimal pH as compared to pH above 6.0. The microbial level decides the amount of benzoate required. Temperature also plays a part; cold-stored juices need less benzoate. Some fruit juices at 30° C require as much as 0.05% to prevent fermentation. Consequently, juice should be kept cool or have lower numbers of yeast organisms. For preservation of a wide variety of foods, sodium benzoate or benzoic acid is used in amounts of less than 0.1 percent.

Sulfur dioxide: Sulfur dioxide is used to treat fruits and vegetables before and after dehydration to extend the storage life of fresh grapes, and to prevent the growth of undesirable microorganisms during winemaking and the manufacture of juices. Sulfur dioxide is more effective against mold spores and bacteria than against yeast; therefore it is combined with sodium benzoate, which is more effective against yeast, for fruit squashes. Sulfur dioxide is also used as a preservative in manufactured meats, sausage, and soft cheeses. In meat the flesh color is stabilized.

Sulfur dioxide is added to dried fruit in amounts up to 3000 ppm; less in dehydrated vegetables. During their storage, sulfur dioxide slows deteriorate changes, such as severe darkening in color and off-flavors. Its reducing action is valuable in preventing the loss of ascorbic acid in dried fruits and vegetables and the disappearance of beta-carotene (pro-vitamin A) in vegetables. Frequently as much as 90 percent sulfur dioxide is removed by steam during the cooking of dried fruits and vegetables.

Sulfur dioxide is usually applied to vegetables after blanching and before dehydration, in the form of Sodium metabisulphite solution. The uses of sulphites, or sulfur dioxide, to treat vegetables prior to dehydration, aids in the prevention of deteriorative changes during dehydration and storage. Sulfur dioxide is a useful agent for the prevention of browning reactions in dried fruits. It should be declared on the label, for those consumers who may be sensitive to it, e.g. people with an asthmatic condition.

Treatment with acid: Most foods may be preserved by heat treatment when they have a pH lower than 4.0. For this reason several methods have been developed which control the pH through the production of acid, or the addition of some organic acid, like acetic, citric and even lactic acid. The acidification of low-acidity vegetables to less than pH 4.5 for commercial sterilization-based processing, with brief sterilization periods at temperatures of 100°C, is a very practical method to employ on a small-scale and even home processing

Raw and processed foods should be packaged to prevent oxidation, microbial contamination, and loss of moisture. Storage of foods (when not contaminated) below -20°C can keep food for several months or a year. Storing foods at 4°C can extend the shelf life to several days or a week (note that some bacteria such as Listeria monocytogenes can still grow and multiply even in foods at refrigerated temperatures).

Today, the demand for processed foods goes beyond the fundamental requirements of safety and shelf-stability. More emphasis is being placed on informatively labeled, high-quality, and value added foods with convenient end use. Improvements in quality and safety of processed foods have been achieved through regulatory requirements on manufacturers, and national or international legislature that recommend and/or enforce performance standards or methods for achieving safety and quality assurance. Equally important is the fact that the need for affordable, yet, high value-added products has been driven by the consumer.

In all its forms of application, thermal processing persists as the most widely used method of preserving and extending the useful shelf life of foods. The concept of in-container sterilization (canning) involves the application of a high-temperature thermal treatment for a sufficiently long time to destroy microorganisms of public health and spoilage concerns. The hermetic seal maintains an environment in the container that prevents the growth of other microorganisms of higher resistance and most importantly, prevents recontamination and pathogens from producing toxins during storage.

Conventional canning operations have the tendency to induce permanent changes to the nutritional and sensory attributes of foods. Therefore, recent developments in food processing operations have aimed at technologies that have the potential to substantially reduce damage to nutrients and sensory components by way of reduced heating times and optimized heating temperatures.

Principles of thermal processing

Thermal destruction of microorganisms is traditionally established to take place following a first order semi-logarithmic rate. Therefore, theoretically, a sterile product cannot be produced with certainty no matter how long is the process time. Targeting a product that is completely void of microorganisms would render the product unwholesome or inferior in quality. Industrially, thermal processes are designed by processing authorities to provide commercially sterile or shelf-stable products. Commercial sterility (as defined by the United States Food and Drug Administration (FDA)) or shelf-stability (U.S. Department of Agriculture (USDA)) refers to conditions achieved in a product by the application of heat to render the product free of microorganisms that are capable of reproducing in the food under normal non-refrigerated conditions of storage and distribution. Designing a sound thermal process requires extensive understanding of process methods, the heating behavior of the product and its impact on a target microorganism. Thus, the severity of any thermal process must be known and depend on factors such as: (i) the physical characteristics of the food product including thermo-physical properties, shape and size of the container holding the product, (ii) the type and thermal resistance of the target microorganisms that are likely to be present in the food, and (iii) the pH, water activity (aw) and salt content of the food. Due to health-related concerns on the use of salt, there is increased demand to reduce salt levels in foods. The United States Food and Drug Administration (FDA) has classified foods in the federal register as follows: (i) acid foods, (ii) acidified foods and (iii) low acid foods. Acid foods are those that have a natural pH of 4.6 or below. Acidified foods (e.g., beans, cucumbers, cabbage, artichokes, cauliflower, puddings, peppers, tropical fruits and fish) are low acid foods to which acid(s) or acid foods are added with a water activity greater than 0.85 and a finished equilibrium pH of 4.6 or below. Low-acid foods have been defined as foods, other than alcoholic beverages, with a finished equilibrium pH greater than 4.6 and a water activity greater than 0.85.

Scientific investigations have revealed that spores of Clostridium botulinum will not germinate and grow in food below pH 4.8. To provide sufficient buffer, a pH of 4.6 has generally been accepted as the point below which C. botulinum will not grow to produce toxin. Thus, a pH of 4.6 represents a demarcating line between low and high acid foods. During thermal processing of low acid foods ($pH \geq 4.6$), attention is given to C. botulinum: the highly heat resistant, rod-shaped, spore former that thrives comfortably under anaerobic conditions to produce the botulism toxin. Commercial sterility is achieved when C. botulinum spores are inactivated to satisfy regulatory requirements. However, other heat resistant spores (generally referred to as thermophiles) such as Clostridium thermosaccolyaticum, Bacillus stearothermophilus, and Bacillus thermoacidurans have the potential to cause spoilage and economic losses when processed cans are stored under “abuse” storage conditions of temperature. The thermophiles would be of no consequence provided one can guarantee that processed cans would be stored at temperatures below 30°C.

Principles of freezing

The freezing process implies two linked processes: (1) lowering of temperature by the removal of heat and (2) a change of phase from liquid to solid. The change of water into ice results in increase in concentration of unfrozen matrix and therefore leads to dehydration and lowering of water activity. Both the lowering of temperature and the lowering of water activity contribute to freezing as an important preservation method.

In order for a product to freeze, the product must be cooled below its freezing point. The freezing point of a food depends on its water content and the type of solutes present. The water component of a food freezes first and leaves the dissolved solids in a more concentrated solution, which requires a lower temperature to freeze. As a result, the freezing point decreases during freezing as concentration increases. Different solutes depress the freezing point to a different degree.

Evaporation and Dehydration

Evaporation: During food processing, evaporation is used to achieve the following goals: (1) concentrate food by the removal of water, (2) remove undesirable food volatiles, and (3) recover desirable food volatiles. Traditionally, evaporation is achieved via the following methods: (1) Use sun energy to evaporate water from seawater to recover the salts left behind. (2) Use a heated kettle or similar equipment to boil water from liquid or semisolid foods (e.g., sugar syrup). (3) An improved method is to evaporate under a vacuum. The term “vacuum evaporator” refers to a closed heated kettle or similar equipment connected to a vacuum pump. One principle to remember is that a major objective of vacuum evaporators is to remove water at temperatures low enough to avoid heat damage to the food.

Drying

Drying differs from evaporating in that the former takes the food to nearly total dryness or the equivalence of 97 or 98% solids. The oldest method of drying food is to put the food under a hot sun. This practice probably started thousands of years ago. Although sun drying is still practiced, especially in many third world countries, modern food drying has been modified to a nearly exact science. Drying has multiple objectives: (1) to preserve the food from spoilage, (2) to reduce the weight and bulk of the food, (3) to make the food enjoy an availability and consumption pleasure similar to that of canned goods, and (4) to develop “new” or “novelty” items such as snacks. Some well-known products prepared from drying include dried milk powder, instant coffee, fish and shell fish, jerky, dried fruits, and dried potato flakes.

Food Additives

One popular method of food preservation uses chemicals, legally known as food additives. The main functional objectives of the use of food additives are (1) to keep bread mold free and salad dressings from separating, (2) to help cake batters rise reliably during baking and keep cured meats safe to eat, (3) to improve the nutritional value of biscuits and pasta and give gingerbread its distinctive flavor, (4) to give margarine its pleasing yellow color and prevent salt from becoming lumpy in its shaker, and (5) to allow many foods to be available year round, in great quantity and the best quality. Food additives play a vital role in today’s bountiful and nutritious food supply. They allow our growing urban population to enjoy a variety of safe, wholesome, tasty foods year-round. And they make possible an array of convenience foods without the inconvenience of daily shopping. Although salt, baking soda, vanilla, and yeast are commonly used in foods today many people tend to think of any food additive as a complex chemical compound. All food additives are carefully regulated by federal authorities and various international organizations to ensure that foods are safe to eat and are accurately labeled. The purpose of this section is to provide helpful background information about food additives, why they are used in foods and how regulations govern their safe use in the food supply.

Additives are used in foods for five main reasons:

1. To maintain product consistency. Emulsifiers give products a consistent texture and prevent them from separating. Stabilizers and thickeners give smooth uniform texture. Anticaking agents help substances such as salt to flow freely.
2. To improve or maintain nutritional value. Vitamins and minerals are added to many common foods such as milk, flour, cereal, and margarine to make up for those likely to be lacking in a person’s diet or lost in processing. Such fortification and enrichment have helped reduce malnutrition in the U.S. population. All products containing added nutrients must be appropriately labeled.
3. To maintain palatability and wholesomeness. Preservatives retard product spoilage caused by mold, air, bacteria, fungi, or yeast. Bacterial contamination can cause food-borne illness, including life-threatening botulism. Antioxidants are preservatives that prevent fats and oils in baked goods and other foods from becoming rancid or developing an off flavor. They also prevent cut fresh fruits such as apples from turning brown when exposed to air.
4. To provide leavening or control acidity/ alkalinity. Leavening agents that release acids when heated can react with baking soda to help cakes, biscuits, and other baked goods to rise during baking. Other additives help modify the acidity and alkalinity of foods for proper flavor, taste, and color.
5. To enhance flavor or impart desired color. Many spices and natural and synthetic flavors enhance the taste of foods. Colors likewise enhance the appearance of certain foods to meet consumer expectations.

V. Packaging of processed and preserved food:

Theory: The main objective of packaging is to keep the fruits, vegetable and root crops in good condition until it is sold and consumed.

- Plastic film bags – widely used for consumer size packs in fruit and vegetables marketing. Retain water vapour so as to reduce H_2O loss from the content.

- Plastic boxes – they are rigid containers most suited for packaging soft and delicate commodities.
- Net / mesh bags – widely used for packing fruits like apple, citrus, guava, sapota etc.
- Sleeve packs – Immobilization of packed fruits, superior visibility that gives a good sales appeal.
- Cling film – Ideal packaging for low water vapour transmission rate, high gas permeability.
- Shrink film or stretch film – Stretching the film under controlled temperature and tension, the film which is wrapped over the produce, stretches and then contract by cooling.
- Active packaging – Also called as smart packaging. It is actively involved with food products or interacts with internal atmosphere to extend shelf life by maintaining quality and safety.
- Antimicrobial packaging – Incorporating antimicrobial agents into polymer surface coating sand surface attachments.
- Wooden packaging – used for packing fruits and vegetable. Similar to plastic crates.
- Modified atmosphere packaging – It is the packaging of a perishable products. The modified atmosphere surrounding the produce beings about the beneficial effects and extends shelf life a products.
- Vacuum packaging – packaging the products in film of low oxygen permeability and sealing it after evacuating the air.
- Teltrapackaging- It is used to store the fruit beverages and RTS beverages
- Bamboo mat holed boxes- Suitable for transportation of apple
- Polypropelene boxes-Highly suitable for long markets it can be reused
- Corrugated fibre board- Suitable for fruit and vegetable and most economical.

For processed fruit and vegetable products:

Aluminium cans, Tin containers, collapsible tubes, glass containers, plastic containers low density polyethylene (LDPE) HDPE, PP (Polypropylene), PVC (Polyviny), chloride, polytysrons (PS), biodegradable plastics, Phetodegradable plastics, laminate, coextruded films, retortable pouch, bulk packaging, aseptic packaging, etc.

VI. Value addition in food products:

The additions of time, place, and/or form utility to a commodity in order to meet the preferences or tastes of the consumer. The true test of value added is achieved when the after tax return on invested capital used to generate time, place, and/or form utility exceeds the overall cost of capital.

Value-added food products are raw or pre-processed commodities whose value has been increased through the addition of ingredients or processes that make them more attractive to the buyer and/or more readily usable by the consumer. It is a production/marketing strategy driven by customer needs and perceptions.

About 15,000 new value-added products are introduced each year. However, getting a new product into the highly competitive retail market is very difficult. USDA estimates that at least two out of every three new food products introduced into the market fail due to lack of customer appeal. Only one in five new businesses succeeds for more than five years. The average time spent on developing new food products is about two years. Product development is not limited to creating new and unique food items. It also includes product repositioning, line extension, and reformulating existing products. Every type of product development consists of five stages: screening, feasibility, costing, prototyping/test marketing, and commercialization.

Value-added is figuring out what consumers want, when they want it, and where they want it-then making it and providing it to them. Thus, value addition in food products will result in nutrient-rich products which have a higher degree of quality, meet the standards set by different authorities and are safer for consumption, having long shelf life, nutritious and easily digestible foods made from different agricultural products are readily available in the market.

Value addition help in nutrient enhancement and reducing the post production losses. Considering the nutritional importance and consumer acceptability, banana flour is used here to develop value added products which is ready to eat and preferred for people of all age groups.

Development of value added products from Banana (Musa paradisiaca L)

OBJECTIVE:

Formulation of different value added products using banana pulp flour and pulp.

MATERIALS AND METHODOLOGY:

1. Collection of samples
2. Preparation of Banana pulp flour
3. Sample preparation
4. Formulation of Biscuit
5. Formulation of Cheela

1. Collection of samples

For carrying out the present study collect required samples from the local market.

2. Preparation of Banana pulp flour

- Collect raw banana
- Wash and peel banana
- Slice and dry the banana
- Grind the dry banana pulp
- Sieve the flour
- Store the flour

3. Sample preparation

3.1 Formation of biscuit

Formulations	**Ingredients used (%)**		**Additional Ingredients (%)**		
	Wheat flour	**Banana flour**	**Sugar**	**Butter**	**Milk**
Formulation 1	60	40	30	30	40
Formulation 2	50	50	30	30	40

The required amount of butter and sugar are taken and mixed together until blended well. The wheat flour and banana flour was added. Then milk was added and all the ingredients were mixed and dough of the biscuit was prepared. The dough is rolled out and cut into desired pieces using cutter. Preheating of oven at 150°C for 5 minutes was done. The biscuits were baked at 150°C for 20-25 minutes or until they were light brown. Then biscuits were cooled and kept in a airtight container.

Weight of the product:

3.2 Formulation of cheela

Formulations	Ingredient used (gm)		Additional ingredients (gm)					
	Besan	Banana flour	Onion	Carrot	Coriander leaves	Salt	Refine oil	Water
Formulation 1	60	40	10	10	8	4	10	100
Formulation 2	50	50	10	10	8	4	10	100

The required amount of besan, banana flour and salt was added. Ingredients were then mixed properly. Further onion, carrot and coriander leaves were added, water was poured and thus the batter was prepared. The pan was heated and then greased lightly with oil. The pan was allowed to turn hot and then flame was reduced to medium. The prepared batter was poured in the pan and spread to a round cheela. It was allowed to cook until the edges leave the pan and then cheela was flipped to the other side. It was fried until cooked completely.

Weight of the product:

VII. Study of Rheology of Jam, Jelly and Sauce:

The food industry requires quick and reliable methods for characterization of properties of industrially produced jams. It was of interest to investigate if it was possible to detect significant differences when the type of pectin in the recipe was changed. Common instruments, capable of measuring fundamental rheological properties of fluid and semi-solid foods, may be placed into two general categories : rotational type and tube type. Most are commercially available, others (mixer and pipe viscometers) are easily fabricated. Rotational instruments may be operated in the steady shear (constant angular velocity) or oscillatory (dynamic) mode. Some rotational instruments function in the controlled stress mode facilitating the collection of creep data, the analysis of materials at very low shear rates, and the investigation of yield stresses. The controlled rate mode is most useful in obtaining data required in process engineering calculations. Rotational systems are generally used to investigate time-dependent behavior because tube systems only allow one pass of the material through the apparatus.

Any processed food material can be classified in terms of response based on their consistency to the external applied load and according to the effects produced in the form of deformation. From a rheological point of view, it is a stand and way to clarify the material behavior depending upon the nature of its response to an external shear stress. A fluid is said to be Newtonian when the flow curve (shear stress v/s shear rate) is linear and it passes through the origin. Such fluids are governed by Newton’s law of viscosity. It is the slope of the flow curve, which characterize the Newtonian material and their proportionality constant is termed as viscosity. Typical examples of Newtonian fluids are air, water, organic liquids, and other low molecular weight substances.

When the flow curve either does not passes through origin or is non-linear, the material is said to be Non-Newtonian. Therefore, the slope of the flow curve for such a material is not a constant and may vary with shear stress or shear rate and in some cases with kinematic history of material element under observation. These Non-Newtonian materials are further classified into several categories. One of the important Non-Newtonian materials are those which are characterized by the existence of a threshold stress, termed as yield stress, σ_γ which must be overcome in order to deform. They are termed as viscoplastic materials. In simple term, they behave like a soft elastic solid when the shear stress is below the yield stress and once the shear stress exceeds the critical value, it behaves like a fluid.

Beyond the yield stress the typical flow curve may be linear or non-linear, but it will never pass through origin. Three prominent viscoplastic models are available in literature (Cheng, 1986). A viscoplastic material with a linear flow curve beyond the yield stress limit is represented by Bingham model as:

$\tau = \tau_y + \mu_\gamma$, For $\tau > \tau_y$

$\gamma = 0$, For $\tau > \tau_y$

where τ is shear stress, τ_y is yield stress μ is apparent viscosity and is shear rate.

An important characteristic of Bingham model is the content viscosity beyond the yield stress. However, there are several viscoplastic materials which shows shear thinning or shear thickening behavior as shown in Fig. 1

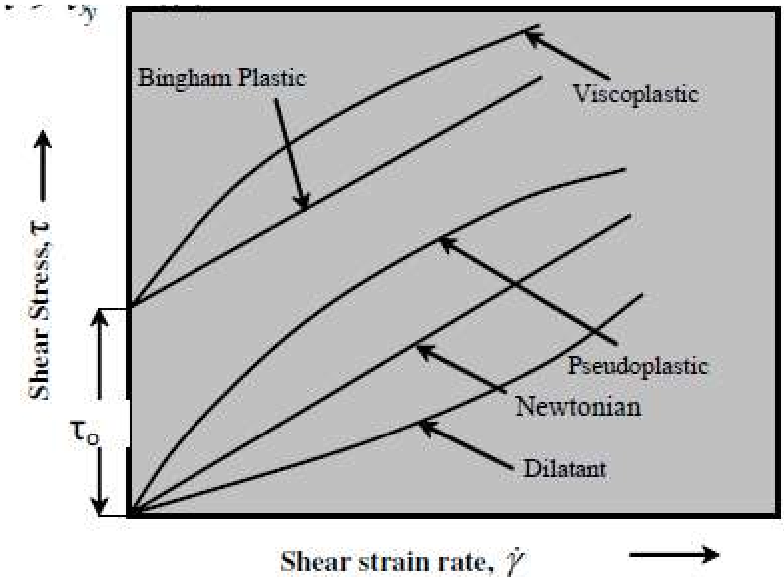


Figure 1. Fluid classification

This nonlinear shearing effect is taken into account by another viscoplastic model known as Herschel-bulkley model represented as:

For

$\gamma = 0$ & , For $\tau < \tau_y$

where n is a power law index that represents the degree of shear thinning or thickening and k is consistency index. In this case the apparent viscosity can be presented as:

$$\eta_{app} = k\,(\dot{\gamma})^{n-1}$$

If n = 1 then Herschel-Bulkley model becomes equivalent to Bingham one. For both Bingham and Herschel-Bulkley models, the curve cross the shear stress axis at the yield stress for a shear rate equal to zero. The direct measurement of yield stress is not possible so it is obtained by extrapolation of flow curve (Cheng, 1986).