QUALITATIVE ANALYSIS OF COMMON CATIONS IN WATER

Muhammad Arif Malik
Hampton University

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Licensing

Dedicated to Mr. Frank Reidy, a philanthropist who brought the author to the US

Mr. Frank Reidy

Dedicated to Mr. Frank Reidy, a philanthropist who brought the author to the US and supported research on the medical application of pulsed electric fields for medical treatments at Frank Reidy Research Center For Bioelectrics, Old Dominion University, Norfolk, VA. The research resulted in developing techniques proven to cure some forms of cancer.

Note for instructors and acknowledgments

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- **Dr. Oluwatoyin Ajibola Asojo** (department chair) for encouraging the author to prepare this book as a free resource for students.

Note for instructors

Suggested plan for executing the experiments: The whole set of experiments is prepared for a duration of almost one semester. The first lab meeting may be reserved to teach the chemistry principles behind the experiments which are in chapter 1. The second lab meeting my be used to introduce the basic experimental techniques in chapter 2 including the demonstration of the techniques by the instructor. Students learning may be assessed through quizzes. Then the students may start to practice the analyses one group of cations at a time.

Students may be asked to complete the first column, "net ionic equations, and observations from the expected reaction", of the datasheet of the relevant group as a pre-lab and couple it with a pre-lab quiz to force the students to understand the experiments before performing them. The post-lab assignment may be filling the second column "actual observations and conclusions" of the relevant datasheet at the completion of the lab activity. Start with the analysis of a known sample containing all ions belonging to the group, followed by a sample containing at least one ion from the group (unknown to students). Group-I analyses can be completed in one lab meeting of about three hours duration. Groups II and III need two lab meetings each. Further, one ion may be removed from groups II and III to save some time, e.g. chromium in group III and tin in group IV may be removed, if needed, as they are relatively difficult for students to identify and the contempt taught through them are repeated in the analyses of some other ions in the same group. Instructors may choose to demonstrate the flame tests in groups IV and V, leaving the analyses of calcium and barium without the flame test for students which can be easily completed in one lab meeting. This approach also minimizes the fire hazard associated with the flame test.

As a lab exam, a sample containing at least one ion from each of the groups I, II, III, and IV (unknown to students) be assigned to each student for the analysis in a time of three to four lab meetings. Students may be asked to fill column 1 of each datasheet again, this time as a pre-lab exam assignment, which may be complemented with a pre-lab exam quiz. Post-lab exam assignment may be filling the second column of the four datasheets as each step of the analysis completes. Tell the students that the data gathered in a lab needs to be discriminated in the form of a scientific report. The data gathered in analytical labs need to be discriminated in the form of a lab report. So, the students may be asked to prepare a lab report based on their findings, systematically explaining the analysis of each ion, supported with reaction equations, what they were expecting to observe, and what their conclusions are supported by the evidence gathered, concluding a summary of the ions identified in the unknown sample.

Preparation of the cation solutions: $Ba(NO_3)_2$, $Ca(NO_3)_2 \cdot 4\,H_2O$, $Cd(NO_3)_2 \cdot 4\,H_2O$, $Cu(NO_3)_2 \cdot 3\,H_2O$, and $Ni(NO_3)_2 \cdot 6\,H_2O$ dissolved in distilled water; $AgNO_3$, $Cr(NO_3)_3 \cdot 9\,H_2O$, $Fe(NO_3)_3 \cdot 9\,H_2O$, (\ce{Cu(NO3)2.6H2O}\), dissolve in 0.1 M HNO_3; $Bi(NO_3)_3 \cdot 5\,H_2O$ dissolves in 3M HNO_3, and $SnCl_4 \cdot 4\,H_2O$ dissolves in 2.5M HCl. Prepare a 0.5M stock solution of each ion needed and then mix the appropriate amount of each with 0.1 M HNO_3 or distilled water, depending on the solubilities of these ions, to make a solution that is 0.1M with respect to each ion in it.

Some cations do not mix well in solution initially. Heat and stir solutions until cations dissolve sufficiently into the solution.

CHAPTER OVERVIEW

1: Chemical Principles

Background to chemical principles involved in the isolation and identification of cations from mixtures are described. Solubility of ionic compounds in water and the solubility variation by common ion effect, pH effect, coordination complex formation, and redox reaction are described in relation to the selective precipitation or dissolution of salts of the cations.

1.1: Solubility

Solution

The **solution** is a homogeneous mixture of two or more substances.

Solution related terminologies

- **Miscible** substances make a solution upon mixing in any proportion. For example, ethanol and water are miscible to each other.
- **Immiscible** substances do not make solutions upon mixing in any proportion.
- **Partially miscible** substances can make a solution upon mixing up to a certain extent but not in all proportions.
- **A solvent** is a larger substance in the solution.
- **A solute** is a small amount of a substance in the solution.
- **An unsaturated solution** is one in which the solvent holds solute less than the maximum limit, i.e., more solute can be dissolved.
- **A saturated solution** is one in which the solvent holds the maximum amount of solute it can dissolve.

Water -a universal solvent

Water is one of the most important solvents because it is present all around us -it covers more than 70% of the earth and more than 60% of our body mass. Water is a polar molecule having a partially negative end on oxygen and a partially positive end on hydrogen atoms. that can dissolve most of the polar and ionic compounds. In ionic compounds, cations are held by anions through electrostatic interaction. When an ionic compound dissolves into water, it dissociates into cations and anions, each surrounded by a layer of water molecules held by ion-dipole interactions. The water molecules around ions make ion-dipole interaction by orienting their partial negative end towards cations and their partial positive end towards anions. The energy needed to break ion-ion interaction in the ionic compounds is partially compensated by the energy released by establishing the ion-dipole interactions. The energy gained due to ion-dipole interactions, and nature's tendency to disperse is the driving forces responsible for the dissolution of ionic compounds.

Solubility

Solubility is the ability of a substance to form a solution with another substance.

The solubility of a solute in a specific solvent is quantitatively expressed as the concentration of the solute in the saturated solution. Usually, the solubility is tabulated in the units of grams of solute per 100 mL of solvent (g/100 mL). The solubility of ionic compounds in water varies over a wide range. All ionic compounds dissolve to some extent.

> For practical purposes, a substance is considered **insoluble** when its solubility is less than 0.1 g per 100 mL of solvent.

For example, lead(II)iodide (PbI_2) and silver chloride ($AgCl$) are insoluble in water because the solubility of PbI_2 is 0.0016 mol/L of the solution and the solubility of $AgCl$ is about 1.3 x 10^{-5} mol/L of solution. Potassium iodide (KI) and $Pb(NO_3)_2$ are soluble in water. When aqueous solutions of KI and $Pb(NO_3)_2$ are mixed, the insoluble combination of ions, i.e., PbI_2 in this case, precipitates, as illustrated in Figure 1.1.1.

Figure 1.1.1: Precipitation reaction: $Pb(NO_3)_2(aq) + 2\,KI(aq) \longrightarrow PbI_2(s)\downarrow + 2\,KNO_3(aq)$. source: PRHaney [CC BY-SA (https://creativecommons).

Solubility guidelines for dissolution of ionic compounds in water

There are no fail-proof guidelines for predicting the solubility of ionic compounds in water. However, the following guidelines can predict the solubility of most ionic compounds.

Soluble ions

1. Salts of alkali metals (Li^+, Na^+, K^+, Rb^+, Cs^+) and ammonia (NH_4^+) are soluble. For example, $NaCl$, and $(NH_4)_3PO_3$ are soluble.
2. Salts of nitrate (NO_3^-), acetate (CH_3COO^-), and perchlorate (ClO_4^-) are soluble. For example, $Pb(NO_3)_2$, and $Ca(CH_3COO)_2$ are soluble.
3. Salts of chloride (Cl^-), bromide (Br^-), and Iodide (I^-) are soluble, except when the cation is Lead (Pb^{2+}), Mercury (Hg_2^{2+}), or Silver (Ag^+). Remember the acronym "LMS" based on the first letter of the element name or phrase 'Let Me See" to recall Lead, Mercury, and Silver.
4. Sulfates (SO_4^{2-}) are soluble except when the cation is, Pb^{2+}, Hg_2^{2+}, or Ag^+ (recall "Let Me See" for Lead, Mercury, and Silver) or a heavy alkaline earth metal ion: calcium (Ca^{2+}), barium (Ba^{2+}), or strontium (Sr^{2+}). (Remember the acronym "CBS" based on the first letter of the element name, or phrase "Come By Soon" to recall calcium, barium, and strontium.)

Insoluble ions

1. Hydroxide (OH^-) and sulfides (S^{2-}) are insoluble except when the cation is a heavy alkaline earth metal ion: Ca^{2+}, Ba^{2+}, or Sr^{2+} (recall "Come By Soon" for calcium, barium, and strontium), alkali metals and ammonium. For example, $Mg(OH)_2$ and CuS are insoluble.
2. Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), and oxide (O^{2-}) are insoluble except when the cation is an alkali metal ion or ammonium. For example, $CaCO_3$, and Fe_2O_3 are insoluble.
3. If there is a conflict between the two guidelines, the first listed guideline has priority. For example, $CaCO_3$ is insoluble (rule#6), but Na_2CO_3 is soluble (rule#1 has priority over rule#6).

Precipitation reactions

Precipitation reactions are a class of chemical reactions in which two solutions are mixed, and a solid product, called a precipitate, separates out. Precipitation reaction happening upon mixing solutions of ionic compounds in water can be predicted as illustrated in Figure 1.1.2. The first step is to list the soluble ionic compounds and then cross-combine the cations of one with the anion of the other to make the potential products. If any of the potential products are insoluble ionic compounds, they will precipitate out. For example, when $NaOH$ solution is mixed with $MgCl_2$ solution, $Mg(OH)_2$ is a cross-combination that forms an insoluble compound, it will precipitate out.

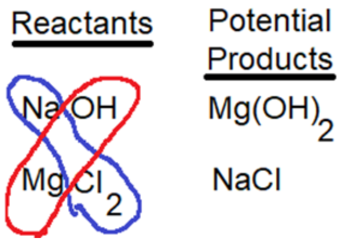


Figure 1.1.2: Cross-combine the cation-anion in the reactants. If any of the cross-combination is an insoluble salt, it will precipitate out, e.g.: $\mathrm{NaOH(aq)} + \mathrm{MgCl_2(aq)} \longrightarrow \mathrm{Mg(OH)_2(s)}\downarrow + \mathrm{NaCl(aq)}$.

Figure 1.1.3 shows precipitates of some insoluble ionic compounds formed by mixing aqueous solutions of appropriate soluble ionic compounds.

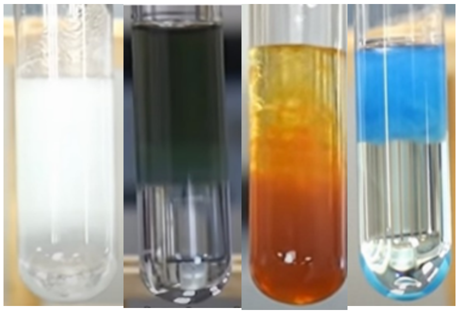


Figure 1.1.3: The precipitates of some insoluble ionic compounds formed by mixing the aqueous solution of appropriate soluble ionic compounds. The precipitates are from left: white Calcium sulfate ($\mathrm{CaSO_4}$), black Iron(II) hydroxide ($\mathrm{Fe(OH)_2}$), brown Iron(III) hydroxide ($\mathrm{Fe(OH)_3}$), and blue Copper(II) hydroxide ($\mathrm{Cu(OH)_2}$). Note that the precipitate is not yet settled at the bottom of the solution; it is still in suspension form in these examples. Source: https://youtu.be/jltLlzZ6FqU

1.2: Solubility equilibria

Solubility product constant (K_{sp})

All ionic compounds dissolve in water to some extent. Ionic compounds are **strong electrolytes**, i.e., dissociating completely into ions upon dissolution. When the amount of ionic compound added to the mixture exceeds the solubility limit, the excess undissolved solute (solid) exists in equilibrium with its dissolved aqueous ions. For example, the following equation represents the equilibrium between solid $\mathrm{AgCl(s)}$ and its dissolved $\mathrm{Ag^{+}(aq)}$ and $\mathrm{Cl^{+}(aq)}$ ions, where the subscript (s) means solid, i.e., the undissolved fraction of the compound, and (aq) means aqueous or dissolved in water.

$$\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^{+}(aq)} + \mathrm{Cl^{-}(aq)}$$

Like any other chemical equilibrium, this equilibrium has an equilibrium constant ($\mathrm{K_{eq}}$) :

$$K_{eq} = [\mathrm{Ag^{+}}][\mathrm{Cl^{-}}]$$

Note that solid or pure liquid species do not appear in the equilibrium constant expression as the concentration in the solid or pure liquid remains constant. This equilibrium constant has a separate name, **Solubility Product Constant** (K_{sp}), based on the fact that it is a product of the molar concentration of dissolved ions, raised to the power equal to their respective coefficients in the chemical equation, e.g.,

$$K_{sp} = [\mathrm{Ag^{+}}][\mathrm{Cl^{-}}] = 1.8 \times 10^{-10}$$

> The solubility product constant (K_{sp}) is the equilibrium constant for an ionic compound dissolving in an aqueous solution.

Similarly, the dissolution equilibrium for $\mathrm{PbCl_2}$ can be shown as:

$$\mathrm{PbCl_2(s)} \rightleftharpoons \mathrm{Pb^{2+}(aq)} + 2\,\mathrm{Cl^{-}(aq)}$$

with

$$K_{sp} = [\mathrm{Pb^{2+}}][\mathrm{Cl^{-}}]^2 = 1.6 \times 10^{-5}$$

And the dissolution equilibrium for $\mathrm{Hg_2Cl_2}$ is similar:

$$\mathrm{Hg_2Cl_2(s)} \rightleftharpoons \mathrm{Hg_2^{2+}(aq)} + 2\,\mathrm{Cl^{-}(aq)}$$

with

$$K_{sp} = [\mathrm{Hg_2^{2+}}][\mathrm{Cl^{-}}]^2 = 1.3 \times 10^{-18}$$

Selective precipitation

> **Selective precipitation** involves adding a reagent that precipitates one of the dissolved cations or a particular group of dissolved cations but not the others.

According to solubility rule# 5, both $\mathrm{Cu^{2+}}$ and $\mathrm{Ni^{2+}}$ form insoluble salts with $\mathrm{S^{2-}}$. However, the solubility of CuS and NiS differ enough that if an appropriate concentration of $\mathrm{S^{2-}}$ is maintained, CuS can be precipitated leaving $\mathrm{Ni^{2+}}$ dissolved. The following calculations based on the K_{sp} values prove it.

$$\mathrm{CuS(s)} \rightleftharpoons \mathrm{Cu^{2+}(aq)} + \mathrm{S^{2-}(aq)}, \quad K_{sp} = [\mathrm{Cu^{2+}}][\mathrm{S^{2-}}] = 8.7 \times 10^{-36}$$

$$\mathrm{NiS(s)} \rightleftharpoons \mathrm{Ni^{2+}(aq)} + \mathrm{S^{2-}(aq)}, \quad K_{sp} = [\mathrm{Ni^{2+}}][\mathrm{S^{2-}}] = 1.8 \times 10^{-21}$$

The molar concentration of sulfide ions $[\mathrm{S^{2-}}]$, in moles/liter in a saturated solution of the ionic compound can be calculated by rearranging their respective K_{sp} expression, e.g., for CuS solution, $K_{sp} = [\mathrm{Cu^{2+}}][\mathrm{S^{2-}}]$ rearranges to:

$$[\mathrm{S^{2-}}] = \frac{K_{sp}}{[\mathrm{Cu^{2+}}]}$$

Assume Cu^{2+} is 0.1 M; plugging in the values in the above equation allows calculating the molar concentration of S^{2-} in the saturated solution of CuS:

$$[\mathrm{S}^{2-}]=\frac{K_{sp}}{[\mathrm{Cu}^{2+}]}=\frac{8.7\times 10^{-36}}{0.1}=8.7\times 10^{-35}\text{~M}$$

Similar calculations show that the molar concentration of S^{2-} in the saturated solution of 0.1M NiS is 1.8 x 10^{-20} M. If S^{2-} concentration is kept more than 8.7 x 10^{-35} M but less than 1.8 x 10^{-20} M, CuS will selectively precipitate leaving Ni^{2+} dissolved in the solution.

Another example is the selective precipitation of Lead, silver, and mercury by adding HCl to the solution. According to rule# 3 of solubility of ionic compounds, chloride Cl^{-} forms soluble salt with the cations except with Lead (Pb^{2+}), Mercury (Hg_2^{2+}), or Silver (Ag^{+}). Adding HCl as a source of Cl^{-} in the solution will selectively precipitate lead (Pb^{2+}), mercury (Hg_2^{2+}), and silver (Ag^{+}), leaving other cations dissolved in the solution.

1.3: Varying solubility of ionic compounds

Le Chatelier's principle

When ionic compounds dissolve in water, they dissociate into ions. An equilibrium is established between the ions in water and the undissolved compound. Changes in the concentration of the ions can stress the equilibrium and vary the solubility of the ionic compounds.

Le Chatelier's principle

Le Chatelier's principle states, “When a system at equilibrium is subjected to a change in concentration, temperature, volume, or pressure, the system will change to a new equilibrium, such that the applied change is partially counteracted.”

If the ions in the solubility equilibrium are increased or decreased by another reaction going on in parallel, the equilibrium will counteract by decreasing or increasing the compound's solubility. The following explains how to use Le Chatelier's principle to vary the solubility of sparingly soluble ionic compounds with examples.

Common ion effect

Consider dissolution of a sparingly soluble ionic compound CaF_2 in water:

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq), \quad K_{sp} = [Ca^{2+}][F^-]^2 = 1.5 \times 10^{-10}$$

The solubility (S) can be expressed in the units of mol/L or molarity (M). Similarly, the concentration of any species in square brackets, as $[Ca^{2+}]$ in the above-mentioned K_{sp} expression, is also in the units of mol/L or M.

NaF is a water-soluble ionic compound that has F^- in common with the above equilibrium. The addition of NaF into the mixture will increase the concentration of F^-, causing a decrease in the solubility of CaF_2 because the solubility equilibrium will move in the reverse direction to counteract the rise in the concentration of the common ion. This is called the **common ion effect**.

> The common ion effect refers to the decrease in the solubility of a sparingly soluble ionic compound by adding a soluble ionic compound with an ion in common with the sparingly soluble one.

A quantitative estimate of this common ion effect is given with the help of the following calculations. If solubility of CaF_2 in pure water is S mol/L, then $[Ca^{2+}]$ = S, and $[F^-]$ = 2S. Plugging in these values in the K_{sp} expression and rearranging shows that the solubility of CaF_2 in pure water is 3.3 x 10^{-4} M:

$$K_{sp} = [Ca^{2+}][F^-]^2$$

$$1.5 \times 10^{-10} = S(2S)^2$$

$$S = \sqrt[3]{1.5 \times 10^{-10}/4} = 3.310^{-4}\ M$$

If F^- concentration is raised to 0.1M by dissolving NaF in the solution, then the molar solubility of CaF_2 changes to a new value S_i , $[Ca^{2+}]$ = S_i, and $[F^-]$ = (0.1 + S_i) = 0.1 (S_i cancels because it is negligible compared to 0.1). Plugging in these values in the K_{sp} expression and rearranging shows that the new solubility (S_i) of CaF_2 is 1.5 x 10^{-8}M:

$$K_{sp} = [Ca^{2+}][F^-]^2$$

$$1.5 \times 10^{-10} = S_i(0.1)^2$$

$$S_i = \frac{1.5 \times 10^{-10}}{(0.1)^2} = 1.5 \times 10^{-8}\ M$$

It means the common ion effect described above decreases the solubility of CaF_2 by more than twenty thousand times.

> Generally, the solubility of sparingly soluble ionic compounds decreases when a common ion is added to the equilibrium mixture.

An example of a common ion effect is in the separation of $PbCl_2$ from $AgCl$ and Hg_2Cl_2 precipitates. $PbCl$ is the most soluble in hot water among these three sparingly soluble compounds. So, $PbCl_2$ is selectively dissolved in hot water and separated. The solution is then cooled to room temperate and HCl is added to it as a source of common ion Cl^- to enforce re-precipitation of $PbCl_2$:

$$Pb^{2+}(aq) + 2\,Cl^-(aq) \rightleftharpoons PbCl_2(s)$$

Effect of pH

The pH is related to the concentration of H_3O^+ and OH^- in the solution. Increasing pH increases OH^- and decreases H_3O^+ concentration in the solution, and decreasing pH has the opposite effect. If one of the ions in the solubility equilibrium of a sparingly soluble ionic compound is an acid or a base, its concentration will change with changes in the pH. It is because acids will neutralize with OH^- at high pH, and bases will neutralize with H_3O^+ at low pH. For example, consider the dissolution of $Mg(OH)_2$ in pure water.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq), \quad K_{sp} = [Mg^{2+}][OH^-]^2 = 2.1 \times 10^{-13}$$

Making the solution acidic, i.e., a decrease in pH adds more H_3O^+ ion that removes OH^- by the following neutralization reaction.

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2\,H_2O(l)$$

According to Le Chatelier's principle, the system moves forward to compensate for the loss of OH^-. In other words, $Mg(OH)_2$ is insoluble in neutral or alkaline water and becomes soluble in acidic water.

> Generally, the solubility of an ionic compound containing basic anion increases by decreasing pH, i.e., in an acidic medium.

In a qualitative analysis of cations, dissociation of H_2S is used as a source of S^{2-} ions:

$$H_2S(g) + 2\,H_2O(l) \rightleftharpoons 2\,H_3O^+(aq) + S^{2-}(aq)$$

The reaction is pH-dependent, i.e., the extent of dissociation of H_2S can be decreased by adding HCl as a source of common ion H_3O^+ or increased by adding a base as a source of OH^- that removes H_3O^+ from the products:

$$OH^-(aq) + H_3O^+(aq) \rightleftharpoons 2\,H_2O(l)$$

> Generally, the solubility of weak acids can be increased by increasing the pH and decreased by decreasing the pH. The opposite is true for the weak bases.

Complex ion equilibria

Transition metal ions, like Ag^+, Cu^{2+}, Ni^{2+}, etc. tend to be strong Lewis acids, i.e., they can accept a lone pair of electrons from Lewis bases. Neutral or anionic species with a lone pair of electrons, like $H_2\ddot{O}:$, $:NH_3$, $:\bar{C}N:$, $:\underset{\cdot\cdot}{\ddot{Cl}}:^-$, etc. can act as Lewis bases in these reactions. The bond formed by donating a lone pair of electrons of a Lewis base to a Lewis acid is called a **coordinate covalent bond**. The neutral compound or ion that results from the Lewis acid-base reaction is called a **coordination complex** or a **complex ion**. For example, silver ion dissolved in water is often written as $Ag^+_{(aq)}$, but, in reality, it exists as complex ion $Ag(H_2O)_2^+$ in which Ag^+ accepts lone pair of electrons from oxygen atoms in water molecules. Transition metal ion in a coordination complex or complex ion, e.g., Ag^+ in $Ag(H_2O)_2^+$ is called **central metal ion** and the Lewis base like $H_2\ddot{O}:$, in $Ag(H_2O)_2^+$, is called a **ligand**. A ligand's strength is its ability to donate its lone pair of electrons to a central metal ion. If a stronger ligand is added to the solution, it displaces a weaker ligand. For example, if $:NH_3$ is dissolved in the solution containing $Ag(H_2O)_2^+$, the $:NH_3$ displaces $H_2\ddot{O}:$ from the complex ion:

$$Ag(H_2O)_2^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + 2\,H_2O(aq)$$

The lone pair on the ligand is omitted from the equation above and the following equations. Water is usually omitted from the equation for simplicity, that reduces the above reaction to the following:

$$\mathrm{Ag^{+}(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^{+}(aq)} \quad K_f = 1.7 \times 10^{7}$$

The equilibrium constant for the formation of complex ion is called **formation constant** (K_f), e.g., in the case of the above reaction:

$$K_f = \frac{[\mathrm{Ag(NH_3)_2^{+}}]}{[\mathrm{Ag^{+}}] \times [\mathrm{NH_3}]^2} = 1.7 \times 10^{7}$$

A large value of K_f in the above reaction shows that the reaction is highly favored in the forward direction. If ammonia is present in water, it increases the solubility of AgCl by removing the $\mathrm{Ag^{+}}$ ion from the products, just like acid ($\mathrm{H_3O^{+}}$) increases the solubility of $\mathrm{Mg(OH)_2}$ by removing $\mathrm{OH^{-}}$ from the products:

$$\mathrm{AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)} \quad K_f = 1.8 \times 10^{-10}$$

$$\mathrm{Ag^{+}(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^{+}(aq)} \quad K_f = 1.7 \times 10^{7}$$

$$\text{Adding above reactions: } \mathrm{AgCl(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^{+}(aq) + Cl^{-}(aq)} \quad K = 3.0 \times 10^{-3}$$

The equilibrium constant for the dissolution of $\mathrm{AgCl}(s)$ changes from 1.8 x 10^{-10} in pure water to 3.0 x 10^{-3} in the water containing dissolved ammonia, i.e., a 17 million times increase. It makes insoluble $\mathrm{AgCl}(s)$ quite soluble. This reaction is used to separate silver ions from mercury ions in a mixture of AgCl and $\mathrm{Hg_2Cl_2}$ mixture precipitates.

> Generally, adding a strong ligand to the solution increases the solubility of metal compounds containing metals capable of coordinate complex formation.

Manipulating chemical equations

The chemical equations can be manipulated like algebraic equations, i.e., multiplied or divided by a constant, added, and subtracted, as demonstrated in the example of the silver ammonia complex formation reactions above. Note that the species on the right side of the equation cancels the same species on the left side of any other equation like algebraic equations, e.g., Ag^{+} is canceled in the final equation.

When two equilibrium reactions are added, their equilibrium constants are multiplied to get the equilibrium constant of the overall reaction, i.e., $K = K_{sp} \times K_f$ in the above reactions.

Redox reactions

There are three major types of chemical reactions: precipitation reactions, acid-base reactions, and redox reactions.

Precipitation reactions

Precipitation reactions of ionic compounds are double replacement reactions where the cation of one compound combines with the anion of another and vice versa, such that one of the new combinations is an insoluble salt.

For example, when silver nitrate ($\mathrm{AgNO_3}$) solution is mixed with sodium chloride (NaCl) solution, an insoluble compound silver chloride (AgCl) precipitates out of the solution:

$$\mathrm{AgNO_3(aq) + HCl(aq) \longrightarrow AgCl(s)\downarrow + NaNO_3(aq)}$$

Acid-base reactions

Acid-base reactions are the reactions involving the transfer of a proton.

For example, $\mathrm{H_2S}$ dissociates in water by donating its proton to water molecules:

$$\mathrm{H_2S(g) + 2\,H_2O(l) \rightleftharpoons 2\,H_3O^{+}(aq) + S^{2\,-}(aq)}$$

Redox reactions

Redox reactions are reactions involving the transfer of electrons.

For example, when sodium metal (Na) reacts with chlorine gas (Cl_2), sodium loses electrons and becomes Na^+ cation and chlorine gains electrons and becomes Cl^- anion that combine to form $NaCl$ salt:

$$2\,Na(s) + 2\,Cl_2(g) \longrightarrow NaCl(s)$$

An example of a redox reaction in qualitative analysis of cations is the dissolution of NiS precipitate by adding an oxidizing acid HNO_3. The S^{2-} is a weak base that can be removed from the product by adding a strong acid like HCl:

$$S^{2-}(aq) + 2\,H_3O^+(aq) \rightleftharpoons H_2S(aq) + 2\,H_2O(l)$$

Therefore, addition of HCl is sufficient to dissolve FS precipitate by removal of S^{2-} from the products:

$$FeS(s) + 2\,H_3O^+(aq) \rightleftharpoons Fe^{2+}(aq) + H_2S(aq) + 2\,H_2O(l)$$

However, the addition of HCl does not remove S^{2-} sufficient enough to dissolve a relatively less soluble NiS precipitate. Nitric acid (HNO_3) that is a source of an oxidizing agent NO_3^- is needed to remove S^{2-} to a higher extent for dissolving NiS:

$$3\,S^{2-}(aq) + 2\,NO_3^-(aq) + 8\,H_3O^+(aq) \longrightarrow 3\,S(s, yellow)\downarrow + 2\,NO(g)\uparrow + 12\,H_2O(l)$$

In this reaction, sulfur is oxidized from an oxidation state of -2 in S^{2-} to an oxidation state of zero in S, and nitrogen is reduced from an oxidation state of +5 in NO_3^- to an oxidation state of +2 in NO.

1.4: pH Buffers

Controlling pH is critically important in the qualitative analysis of cations. Often, pH needs to be maintained in a narrow range.

> A **pH buffer** is an aqueous solution consisting of a weak acid and its conjugate base or vice versa. It minimizes the pH change when a small amount of a strong acid or a strong base is added to it.

For example, adding 0.020 mol HCl into 1 L of water changes pH from 7 to 1.7, i.e., about 80% change in pH. Similarly, adding 0.020 mol NaOH to the same water changes pH from 7 to 12.3, i.e., about 80% change in pH. In contrast to pure water, 1 L of buffer solution containing 0.50 mol a week acid acetic acid $(\mathrm{CH_3COOH})$ and 0.50 mol of its conjugate base $\mathrm{CH_3COO^-}$ changes pH from 4.74 to 4.70 by the addition of the same 0.020 mol HCl and from 4.74 to 4.77 by the addition of 0.020 mol NaOH, i.e., about 1% change in pH, as illustrated in Fig. 1.7.1.

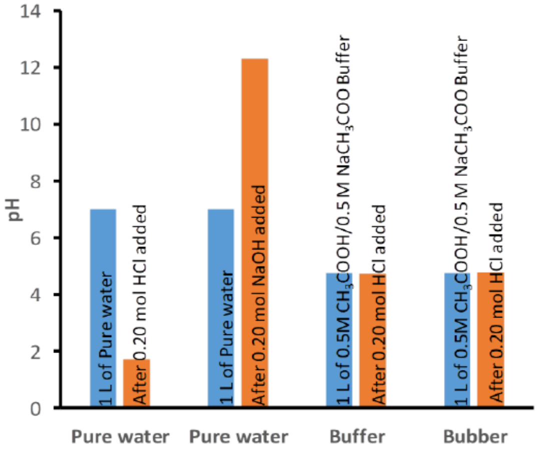


Figure 1.4.1: Effect of acid and base addition on pH change of pure water at pH 7.00 and acetic acid/sodium acetate buffer at pH 4.74.

The buffer contains a weak acid and its conjugate base in equilibrium. For example, **acetic acid/sodium acetate buffer** has the following equilibrium:

$$\mathrm{CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-}$$

The molar concentration of hydronium ions $[\mathrm{H_3O^+}]$ defines the pH of the solution, i.e., $\mathrm{pH} = -\log\left[\mathrm{H_3O^+}\right]$. The conjugate base consumes any strong acid added to the mixture:

$$\mathrm{HA + CH_3COO^- \longrightarrow CH_3COOH + A^-}$$

, where HA is any strong acid and $\mathrm{A^-}$ is its conjugate base. The concentration of $\mathrm{CH_3COOH}$ increases and $\mathrm{CH_3COO^-}$ decrease, but pH decreases little because $[\mathrm{H_3O^+}]$ is almost not affected. Similarly, the weak acid consumes any strong base added.

$$\mathrm{MOH + CH_3COOH \longrightarrow CH_3COO^- + M^+ + H_2O}$$

, where $\mathrm{M^+}$ is its conjugate acid. The concentration of $\mathrm{CH_3COOH}$ decreases and $\mathrm{CH_3COO^-}$ increases, but pH increases little because $[\mathrm{H_3O^+}]$ is almost not affected. Buffers are employed on several occasions during the qualitative analysis of cations.

1.5: Separation of cations in groups

Steps in the qualitative analysis of cations in water

Qualitative analysis of cations commonly found in water solution is usually done in three stages:

1. ions are separated into broader groups by selective precipitation based on their solubility properties,
2. member ions in a group are separated usually by selective dissolution of the precipitates and
3. a specific confirmation test identifies individual ions.

For the 1st stage, i.e., separation of cations in groups, a suitable reagent is selected that selectively precipitates certain ions leaving the rest of the ions in the solution.

Criteria for selecting a suitable reagent for the selective precipitation

A suitable reagent is the one that:

1. almost completely removes the ions belonging to the group so that the residual ions may not interfere with the analysis of the other ions left in the solution,
2. should not precipitate out a fraction of ions that do not belong to the group being separated, and
3. should not leave behind counter ions that can interfere with the analysis of the rest of the ions.

> The reagents are added in an order such that the most selective reagent, the one that precipitates out the least number of ions, is added first.

The fourteen common cations found in water that are selected in these exercises are separated into five groups.

Group I comprises lead II (Pb^{2+}), mercury (I) (Hg_2^{2+}), and silver (I) (Ag^{+}) that are selectively precipitated as chlorides by adding 6M HCl to the mixture.

$$HCl + H_2O(l) \longrightarrow H_3O^{+}(aq) + Cl^{-}(aq)$$

> HCl solution is selected as a reagent for group I based on the facts: i) it is a source of chloride (Cl^{-}) ion which is the most selective reagent that makes insoluble salts with only Pb^{2+}, Hg_2^{2+}, and Ag^{+} (recall soluble ions rule#3 described in section 1.1), ii) it leaves behind H_3O^{+} that makes the solution acidic which is beneficial for separation of cations of the next group.

Group II comprises tin(IV) (Sn^{4+}), cadmium(II) (Cd^{2+}), copper(II) (Cu^{2+}), and bismuth(III) (Bi^{3+}) that are selectively precipitated as sulfides by adding H_2S reagent in an acidic medium. H_2S is a source of sulfide (S^{2-}) ion in water:

$$H_2S(aq) + 2\,H_2O(l) \longrightarrow 2\,H_3O^{+}(aq) + S^{2-}(aq)$$

The S^{2-} ion makes insoluble salts with many cations as stated by insoluble ions rule#1 in section 1.1, i.e., "Hydroxide (OH^{-}) and sulfides (S^{2-}) are insoluble except when the cation is a heavy alkaline earth metal ion: Ca^{2+}, Ba^{2+}, and Sr^{2+}, or an alkali metal ion, or ammonia."

> H_2S in acidic medium is selected as a source of S^{2-}, which is the reagent for selective precipitation of group II, because the concentration of S^{2-} can be controlled by adjusting pH. Acidic medium has higher $[H_3O^{+}]$ that decreases S^{2-} due to the common ion effect of H_3O^{+} ion. Therefore, only the group II cations with very low solubility are selectively precipitated among the sulfide insoluble salts.

Group III comprises chromium(III) (Cr^{3+}), iron(II) (Fe^{2+}), iron(III) (Fe^{3+}), and nickel(II) (Ni^{2+}) selectively precipitated as insoluble hydroxides and sulfides by adding H_2S in alkaline medium with pH maintained at ~9 by NH_3/NH_4^{+} buffer.

> H_2S in an alkaline medium is the reagent for the selective precipitation of group III cations.

When pH is set at 9 by NH_3/NH_4^+ buffer, OH^- concentration is high enough to precipitate group III cations as insoluble hydroxide except for nickel that forms soluble coordination complex ion with ammonia. When H_2S is added in an alkaline medium, it produces a higher concentration of S^{2-} due to the removal of H_3O^+ from its equilibrium by reacting with OH^-:

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2\,H_2O(l)$$

All of the group III cations are converted to insoluble sulfides except chromium.

Group IV comprises of calcium (Ca^{2+}) and barium (Ba^{2+}) selectively precipitate as insoluble carbonates by adding ammonium carbonate ($(NH_4)_2CO_3$) as a source of carbonate (CO_3^{2-}) ion:

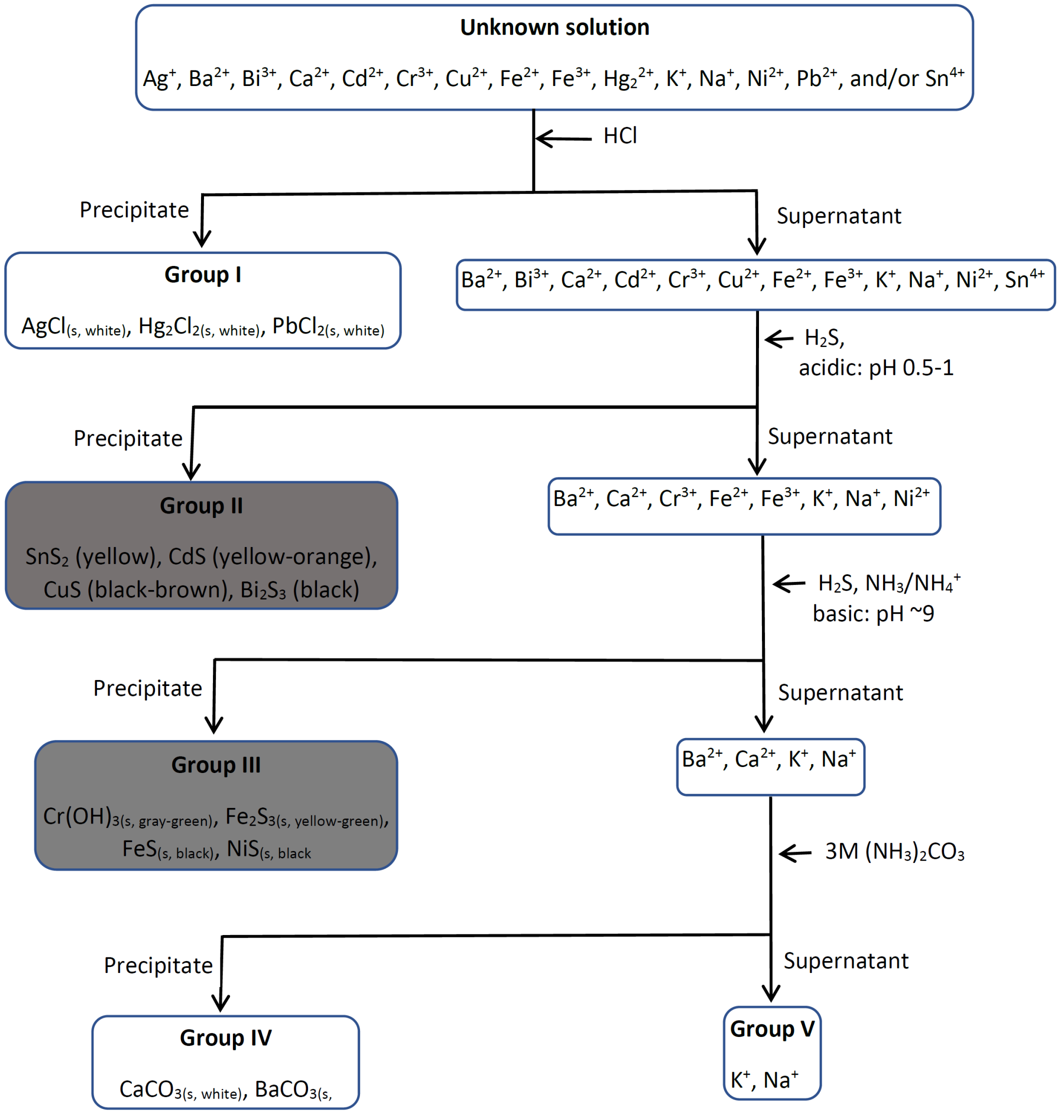
$$(NH_4)_2CO_3(s) + 2\,H_2O \rightleftharpoons 2\,NH_4^+(aq) + CO_3^{2-}(aq)$$

The CO_3^{2-} ion makes insoluble salts with many cations as stated by insoluble ions rule#2 in section 1.1, i.e., “Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), and oxide (O^{2-}) are insoluble except when the cation is an alkali metal ion or ammonia.” All other ions have already been precipitated in groups I, II, and III except group IV cations and alkali metal ions.

> The CO_3^{2-} ion is a selective reagent for group IV cations.

Group V comprises alkali metal ions, i.e., sodium (Na^+) and potassium (K^+) in the mixture of ions selected. According to soluble ions rule#1 in section 1.1, alkali metal and ammonium ions form soluble salts. So, group V cations remain in solution after groups I, II, III, and IV are removed as insoluble, chloride, sulfide in acid medium, sulfide in basic medium, and carbonates, respectively.

Later chapters describe in detail the separation of cations in groups, the separation of ions within a group, and their confirmation tests. The flow chart shown below summarizes the separation of common cations in water into five groups.


Unknown solution
Ag^+, Ba^{2+}, Bi^{3+}, Ca^{2+}, Cd^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg_2^{2+}, K^+, Na^+, Ni^{2+}, Pb^{2+}, and/or Sn^{4+}
HCl
Precipitate
Supernatant
Group I
$AgCl_{(s,\ white)}$, $Hg_2Cl_{2(s,\ white)}$, $PbCl_{2(s,\ white)}$
Ba^{2+}, Bi^{3+}, Ca^{2+}, Cd^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^+, Na^+, Ni^{2+}, Sn^{4+}
H_2S,
acidic: pH 0.5-1
Precipitate
Supernatant
Group II
SnS_2 (yellow), CdS (yellow-orange),
CuS (black-brown), Bi_2S_3 (black)
Ba^{2+}, Ca^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, K^+, Na^+, Ni^{2+}
H_2S, NH_3/NH_4^+
basic: pH ~9
Precipitate
Supernatant
Group III
$Cr(OH)_{3(s,\ gray\text{-}green)}$, $Fe_2S_{3(s,\ yellow\text{-}green)}$,
$FeS_{(s,\ black)}$, $NiS_{(s,\ black}$
Ba^{2+}, Ca^{2+}, K^+, Na^+
3M $(NH_3)_2CO_3$
Precipitate
Supernatant
Group IV
$CaCO_{3(s,\ white)}$, $BaCO_{3(s,}$
Group V
K^+, Na^+

CHAPTER OVERVIEW

2: Experimental techniques

2.1: Precipitation

The chemical reactions in these exercises are performed in a test tube. Test tubes come in different sizes. These experiments are designed for test tubes of 9 mL capacity. The reactant is in a test tube and the reagent (2nd reactant) is added drop by drop from a reagent bottle using a dropper, while the reaction mixture is being stirred. Use a clean glass rod to stir the reaction mixture. Stirring is necessary as the reactants must mix before they can react. Figure $2.1.1$ illustrates the test tubes and reagent bottles commonly used.

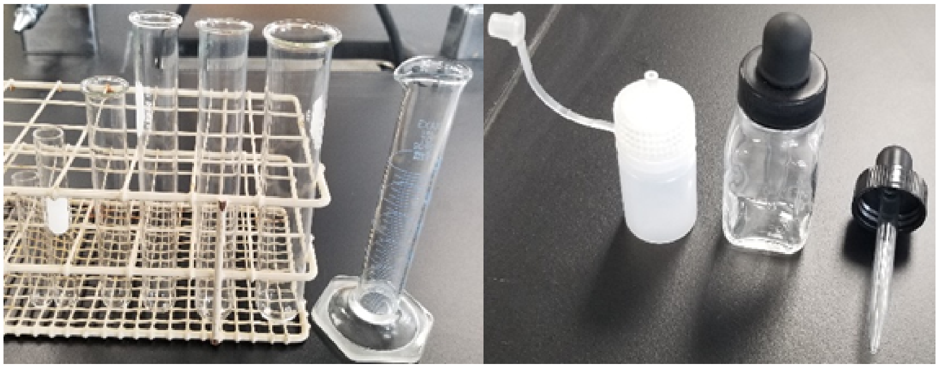


Figure $2.1.1$: Test tubes of different sizes and a 25 mL capacity graduated cylinder (left) and reagent bottles with a dropper fitted in the cap (right).

- Dissolved compounds make a clear solution, i.e., the solution may be colored but it is transparent (not opaque) -it remains see-through.
- In a precipitation reaction, the solid product separates out from the clear solution making the solution opaque or turbid called a **suspension**.
- The solid product i.e., **precipitate**, may be filtered out, but usually, it is forced to settle at the bottom of the test tube as **sediment** or a **solid pellet**, by centrifugation process leaving a clear solution, i.e., **supernatant**, at the top.

Figure $2.1.2$ illustrated a precipitation reaction and the difference between solution, suspension, supernatant, and precipitate.

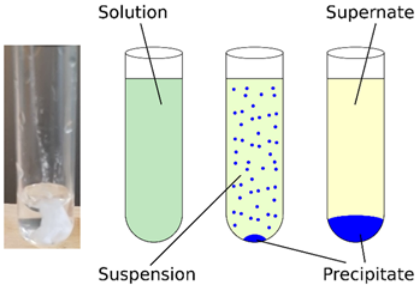


Figure $2.1.2$: Formation of a milky-white AgCl precipitate upon addition of HCl to $AgNO_3$ solution and illustration of a solution, suspension, and precipitation. (Attributes for the illustration: ZabMilenko: orginalZooFari: vectorMrmw: optimized, multilang, CC0, via Wikimedia Commons)

Precipitation reaction must be tested for completeness, as, otherwise, the residual reactant will interfere with the other tests to be performed using the supernatant. One more drop of reagent is added to the clear supernatant and if no more precipitate forms the precipitation is complete. Otherwise, repeat the centrifugation and check again.

2.2: Water bath

Often a reaction mixture needs to be heated for a certain time for the reaction to happen. Heating directly on a Bunsen burner or on a hot plate is not uniform heating is associated with fire hazards. Heating the reaction mixture indirectly in a water bath achieves uniform heating with less fire hazard.

Lab water bath setup

A water bath for qualitative analysis of cations is usually a 200 mL capacity beaker filled with distilled or deionized water up to about 150 mL mark and placed on a hot plate for heating. Ramp up the temperature control knob of the hot plate to a maximum in the beginning until the water starts boiling. Then set the temperature to 350 °C to keep it gently boiling as illustrated in Figure 2.2.1. Add water when the water level drops to the range ½ to 1/4th, ramp up temperature again, and then re-set the temperature at 350 °C once it starts boiling again.

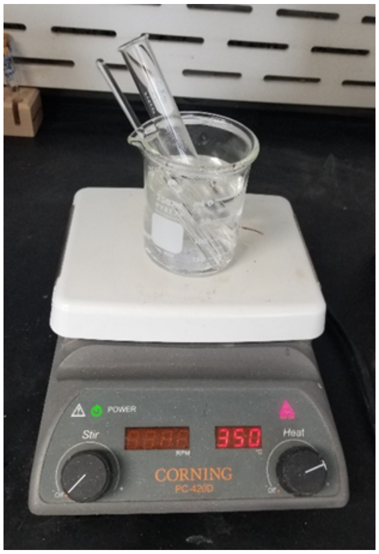


Figure 2.2.1: Water bath prepared for heating reactants in a test tube.

Caution

Hold the hot test tube with a test tube holder while stirring with a clean glass rod or while moving it to centrifuge. Never hold the hot test tube with a bare hand. Always point the mouth of the hot test tube away from you and away from any other person around. Hot test tubes and the hot liquid in the test tube can cause burns.

2.3: Centrifugation

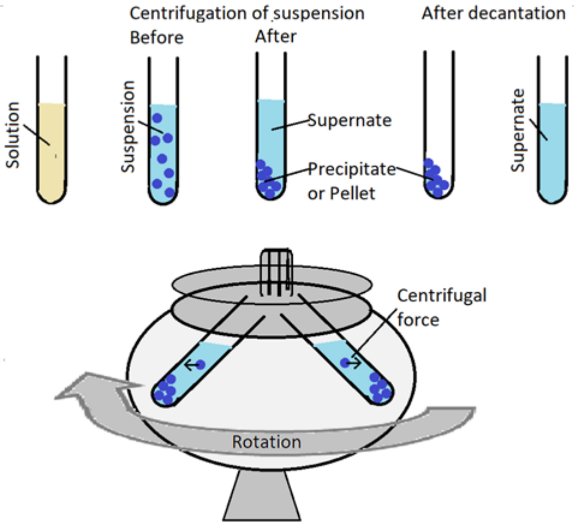


Figure 2.3.1: Illustration of separation of supernatant from the precipitate by centrifugation process.

The solid product, i.e., the precipitate is forced to form sediment or pellet at the bottom of the test tube under the action of centrifugal force as illustrated in Figure 2.3.1. A laboratory centrifuge machine contains a fast router with compartments to house the test tube as shown in Figure 2.3.2. The test tube compartments are arranged in a circle.

- Always place two test tubes across the diagonal, one containing the solution of interest and the other similar test tube containing an equal volume of water to counterbalance the weight.

Three similar test tubes with the same volume of liquid can also be placed at the corner of a triangle around the axis of the router to balance the weight. Close the lid and start the machine. If the weight is not balanced, the centrifuge machine will vibrate, shake, and may start moving or fly off causing damage when switched on.

Caution

- Always keep eye on the centrifuge when it starts -if there is any abnormal sound, shaking, or vibration, immediately switch off or unplug the centrifuge machine. When the centrifuge machine is unplugged or switched off, the router keeps running for a while before coming to stop. Never open the lid until the router comes to a complete stop.

Figure 2.3.2: A laboratory centrifuge machine with the lid open (left), router compartment showing test tubes placed across to balance the weight (middle), centrifuge ready to start with a sample loaded, and the lid closed.

2.4: Separation of the precipitate

Decantation and aspiration

After centrifugation, a clear liquid, called supernatant, is floating over the sediment or precipitate. Figure 2.4.1 shows the separation of supernatant from the precipitate by decantation and by aspiration.

- The supernatant is removed by **decantation**, i.e., by pouring out the supernatant.
- A pasture pipette can also be used to draw out the supernatant -a process called **aspiration**.

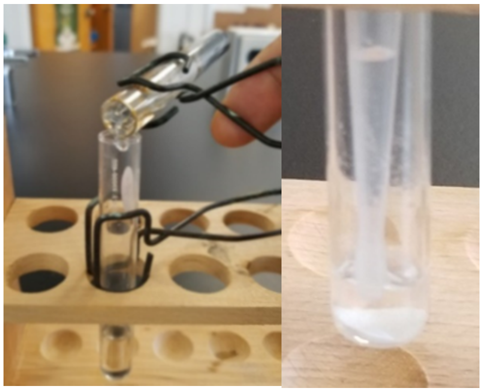


Figure 2.4.1: Decantation, i.e., pouring out the supernatant (left) and aspiration, i.e., carefully draw out the clear supernatant from a tightly packed precipitate using a pasture pipette (right).

Cotton-plug technique in aspiration

Sometimes the precipitate is not fully packed after centrifugation and tends to go into supernatant during the decantation or aspiration process. In these situations, a cotton-plug technique is used, i.e., a small tuft of cotton is twisted at one end between fingers to make it pointy at one end. Then the pointy end is plugged into the tip of a pasture pipette to act as a filter during aspiration. The loose precipitate is filtered by the cotton plug during aspiration as illustrated in Figure 2.4.2. The cotton plug is removed and then the clear supernatant is transferred to a clean test tube for further analysis.

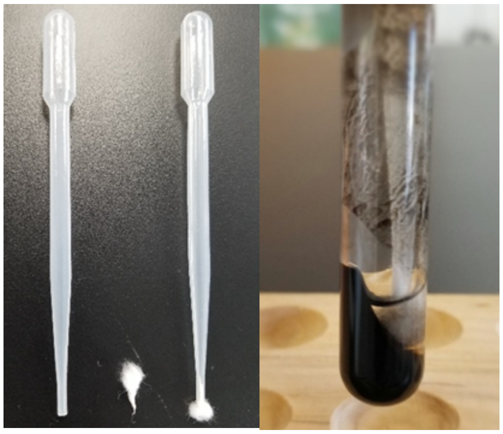


Figure 2.4.2: Cotton plug technique, from left to right: i) a Pasteur pipette, ii) a cotton tuft made pointy at one end, iii) a Pasteur pipette with cotton-plug fitted in the tip, and iv) aspiration from a loosely packed precipitate using cotton plug technique.

Washing the precipitate

The precipitate is usually washed by re-suspending by stirring with a clean glass rod in a solvent that does not re-dissolve the product but dissolves any impurity in it, as shown in Figure 2.4.3. The suspension is centrifuged or gravity filtered and the supernatant or filtrate of the washing step is discarded as it is just the washing liquid with some impurities in it.

Figure 2.4.3: Precipitate re-suspended in a washing solvent.

Gravity filtration

Sometimes a precipitate in a suspension is separated by gravity filtration. A gravity filtration setup consists of a funnel placed in a test tube or an Erlenmeyer flask and a filter paper placed in the funnel as illustrated in Figure 2.4.4. Suspension is poured into the filter paper. The solution that passes through the filter paper and is collected in the test tube or Erlenmeyer flask is called the **filtrate**. The precipitate that is retained on the filter paper is called the **residue**.

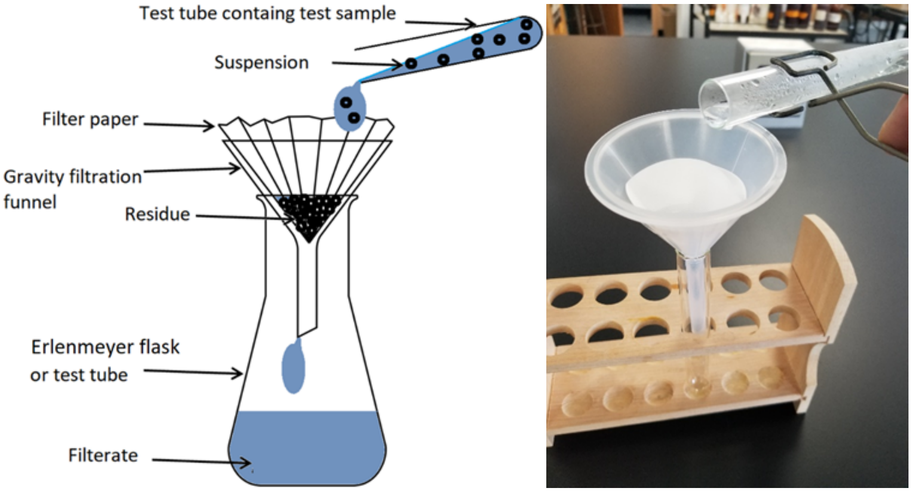


Figure 2.4.4: Illustration of a gravity filtration setup (left) and a gravity filtration setup being heated with hot water to prepare it for heated gravity filtration (right).

The precipitate is washed by adding a washing solution drop by drop while gently stirring the residue with a clean glass rod.

Caution

- Stir the residue very gently as otherwise the wet filter paper my rupture. The room temperature gravity setup is converted to a heated gravity filtration setup by pouring hot water into the filter paper and discarding the filtrate which is just the hot water.

2.5: pH measurement

The pH is usually measured in laboratories by a digital pH meter. The electrode of the pH meter is first calibrated with solutions of know pH values, and then the electrode is dipped in the test solution to read its pH value.

pH papers are a cheaper alternative often used for pH measurement in qualitative analyses of cations that gives quick results, as illustrated in Figure $2.5.1$.

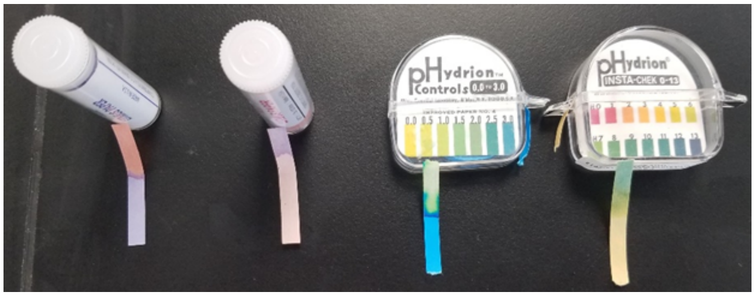


Figure $2.5.1$: Illustration of pH measurements, from left to right: i) blue litmus paper turned red a the top end by an alkaline solution, ii) red litmus paper turned blue at the top end by an alkaline solution, iii) short-range pH paper testing a solution of pH ~0.5, and iv) full range pH paper testing a solution at pH ~8.

Using a pH paper

If the purpose is to monitor when the solution turns from acidic to alkaline or vice versa, a litmus paper is used. A red litmus paper stays red in an acidic solution and turns blue in a basic solution. A blue litmus paper turns red in acidic and stays blue in a basic solution.

If the purpose is to determine an approximate pH value, a universal pH indicator paper is used. The test solution is applied to the end of a pH paper strip with a glass rod and the pH is read by matching the color of the test paper socked in the test solution with the color chart on the pH paper box.

Caution

A common mistake is dipping a pH paper in the test solution and withdrawing immediately to read the color change. It should be avoided as it may leave contaminants in the solution. Further, the test solution is at the bottom of the test tube requiring a long paper strip and making it difficult to avoid touching the sides of the test tube above the liquid. A better approach is to cut a piece of pH paper about 2 cm long and touch one end with a wet glass rod that was used to stir the test solution and then read the color change in the pH paper by matching it to the color on the chart.

2.6: Flame test

A flame test is a complex phenomenon that is not fully explained. In simple words, when a solution of metal salts, e.g., an aqueous solution of metal chlorides is injected into a flame, some of the metal ions may gain electrons and become neutral metal atoms. Electrons in the atom can be promoted from the ground state to a higher energy excited state by the strong heat of the flame. The excited electrons ultimately return to the ground state either in one go or in several steps by jumping to lower allowed energy states. When the excited electrons jump from higher to lower allowed energy states they emit electromagnetic radiation of a specific wavelength corresponding to the energy gap between the energy states. Some of these radiations may fall in the visible part of the electromagnetic radiation spectrum. The color we see is a combination of all the colors in the emission spectrum, as illustrated in Fig. 2.7.1.Figure $2.6.1$.

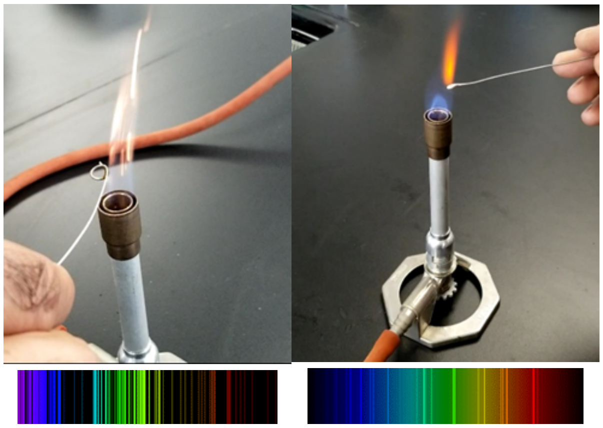


Figure $2.6.1$: Flame colors using a nichrome wire (top) and the corresponding emission spectra (bottom) of iron chloride (left) and calcium chloride solutions in water (right). Emission spectra are taken from Wikipedia/commons, license: public domain (Creative Commons CC0)

The exact gap between the energy levels allowed for electrons varies from one metal to another metal. Therefore, different metals have different patterns of spectral lines in their emission spectrum, and if some of these spectral lines fall in the visible spectrum range, they impart different colors to the flame. For example, the ground-state electron configuration of the sodium atom is $1s^2 2s^2 2p^6$. When the sodium atom is in the hot flame some of the electrons can jump to any of the higher energy allowed stages, such as 3s, 3p, etc. The familiar intense yellow flame of sodium is a result of excited electrons jumping back from $3p^1$ to ground state $3s^1$ level.

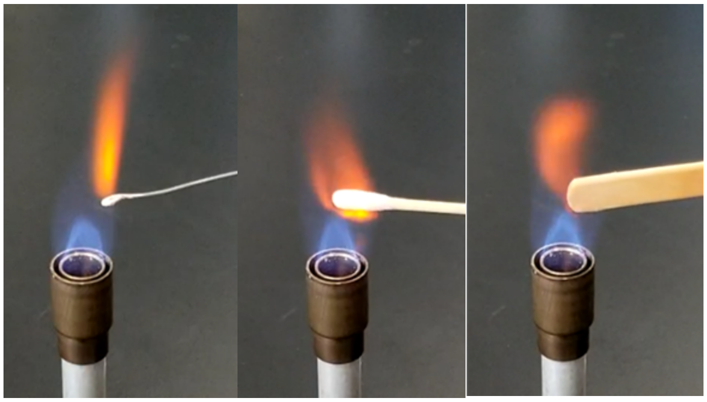


Figure $2.6.2$: Calcium flame test using a nichrome wire (left), a cotton-tipped swab (middle) and a wooden splint (right)

Flame test procedure

Often metal chloride salts are used for the flame tests as they are water-soluble and easier to vaporize in flame from the solution. Metal chloride salts are first dissolved in water. Other metal salts are first treated with 6M HCl to dissolve them as metal chlorides and then used for the flame test. An inert platinum wire is dipped in the test solution. Usually, the wire has a small loop a the end to make a film of the solution that evaporates in the flame. Air and fuel supply to the flame are adjusted to produce a non-luminous flame. The wire carrying the salt solution is touched on the outer edge of a flame somewhere in the middle of the vertical axis of the flame and the color imparted to the flame is observed. Nichrome wire is a cheaper alternative to platinum wire, though nichrome may slightly alter the flame color. A wooden splint or wooden cotton-tipped applicator are other cheaper alternatives. The wooden splint or cotton swab applicator is first dipped in deionized or distilled water overnight so that the cotton or wood may not burn when placed in a flame for a short time. The salt solution is then applied to the wooden splint end or to the cotton swab and exposed to the flame.

Wooden splint and cotton-tipped applicators are disposable, i.e., they are discarded after one flame test. Platinum wire can be reused after washing. The wire is dipped in 6M HCl and then heated in a flame to red-hot. The process is repeated till the wire does not alter the color of the flame. Then it can be re-used. Nichrome wire can be washed the same way. However, an easier alternative is to cut out the loop of the wire and make a new loop on the fresh end portion. Then use the wire for the next flame test.

Figure $2.6.2$ shows that flame tests tested using calcium chloride work equally well with nichrome wire, cotton-tipped applicator, and wooden splint. Figure $2.6.3$ shows flam colors of some metal chloride salt solutions exposed to the flame on a cotton swab applicator.

Figure $2.6.3$: Flame test colors, from left to right: red $CaCl_2$, blue $CuCl_2$, red $LiCl$, yellow NaCl, purple KCl, red $SrCl_2$, folder sparkly $FeCl_3$, and yellow-green $BaCl_2$. Source: taken from a YouTube video contributed by Step by Step Science.

2.7: Common qualitative analysis reagents, their effects, and hazards

Common qualitative analysis reagents, their effects, and hazards

Reagent	Effects	Hazards
6M Ammonia (NH_4OH or NH_3)	increases $[NH_3]$, increases $[OH^-]$, decrease $[H_3O^+]$, precipitates insoluble hydroxides, forms NH_3 complexes	Toxic, corrosive, and irritant
6M Hydrochloric acid (HCl)	increases $[H_3O^+]$, increases $[Cl^-]$, decreases $[OH^-]$, dissolves insoluble carbonates, chromates, hydroxides, some sulfates, destroys hydroxo and NH_3 complexes, and precipitates insoluble chlorides	Toxic and corrosive
3% Hydrogen peroxide (H_2O_2)	Oxidizing agent in acidic medium, reducing agent in basic medium	corrosive
6M Nitric acid (HNO_3)	Increases $[H_3O^+]$, decreases $[OH^-]$, dissolves insoluble carbonates, chromates, and hydroxides, dissolves insoluble sulfides by oxidizing sulfide ion, destroys hydroxo and ammonia complexes, good oxidizing agent when hot	Toxic, corrosive, and strong oxidant
3M Potassium hydroxide (KOH)	Increases $[OH^-]$, decreases $[H_3O^+]$, forms hydroxo complexes, precipitates insoluble hydroxides	Toxic and corrosive
1M Thioacetamide ($CH_3C(S)NH_2$)	Produces H_2S, i.e., a source of sulfide ion (S^{2-}), precipitates insoluble sulfides	Toxic and carcinogen

CHAPTER OVERVIEW

3: Group I cations

3.1: Separation of group I cations

Selective precipitation of a set of group I, i.e., lead(II) (Pb^{2+}), mercury(I) (Hg_2^{2+}), and silver(I) (Ag^+) is based on soluble ions rule#3 in the solubility guidelines in section 1.1 which states "Salts of chloride (Cl^-), bromide (Br^-), and Iodide (I^-) are soluble, except when the cation is Lead (Pb^{2+}), Mercury (Hg_2^{2+}), or Silver (Ag^+). The best source of Cl^- for precipitating group 1 cations from a test solution is HCl, because it is a strong acid that completely dissociates in water producing Cl^- and H_3O^+ ions, both do not get involved in any undesired reactions under the conditions.

The K_{sp} expression is used to calculate Cl^- that will be sufficient to precipitate group 1 cations. The molar concentration of chloride ions i.e., $[Cl^-]$, in moles/liter in a saturated solution of the ionic compound can be calculated by rearranging their respective K_{sp} expression. For example, for AgCl solution, $K_{sp} = \left[Ag^+\right]\left[Cl^-\right]$ rearranges to:

$$\left[Cl^-\right] = K_{sp} / \left[Ag^+\right]$$

and for $PbCl_2$ solution, $K_{sp} = [Pb^{2+}][Cl^-]^2$ rearranges to:

$$\left[Cl^-\right] = \sqrt{K_{sp} / \left[Pb^{2+}\right]}$$

The concentration of ions in the unknown sample are ~0.1 M. Plugging in 0.1M value for Pb^{2+} in the above equation shows that [Cl^-] in a saturated solution having 0.1M Pb^{2+} is 1.3 x 10^{-2}M:

$$\left[Cl^-\right] = \sqrt{K_{sp} / \left[Pb^{2+}\right]} = \sqrt[2]{1.6 \times 10^{-5} / 0.1} = 1.3 \times 10^{-2}\,\mathrm{M}$$

It means Cl^- concentration up to 1.3 x 10^{-2}M will not cause precipitation from 0.1M Pb^{2+} solution. Increasing Cl^- above 0.013M will remove Pb^{2+} from the solution as a $PbCl_2$ precipitate. If 99.9% removal is desired, then 1.0 x 10^{-4} M Pb^{2+} will be left in the solution and the $[Cl^-]$ have to be raised to 0.40 M:

$$\left[Cl^-\right] = \sqrt[2]{K_{sp} / \left[Pb^{2+}\right]} = \sqrt[2]{1.6 \times 10^{-5} / 1.0 \times 10^{-4}} = 0.40\mathrm{M}$$

The solubility of Hg_2Cl_2 and AgCl is less than that of $PbCl_2$. So, a 0.40M Cl^- will remove more than 99.9% of Hg_2^{2+} and Ag^+ from the solution.

A sample of 20 drops of the aqueous solution is about 1 mL. In these experiments, ~15 drops of the test solution are collected in a test tube and 3 to 4 drops of 6M HCl are mixed with the solution. This results in about 0.9 mL total solution containing 1 to 1.3 M Cl^-, which is more than twice the concentration needed to precipitate out 99.9% of group 1 cations.

A concentrated reagent (6M HCl) is used to minimize the dilution of the test sample because the solution is centrifuged and the supernatant that is separated by decantation is used to analyze the remaining cations. A 12M HCl is available, but it is not used because it is a more hazardous reagent due to being more concentrated strong acid and also because if Cl^- concentration is raised to 5M or higher in the test solution, it can re-dissolve AgCl, by forming water-soluble $[AgCl_2]^-$ complex ion.

The addition of HCl causes precipitation of group 1 cation as milky white suspension as shown in Figure 3.1.1 and by chemical reaction equations below. The precipitates can be separated by gravity filtration, but more effective separation can be achieved by subjecting the suspension to centrifuge in a test tube. Centrifugal force forces the solid suspension to settle and pack at the bottom of the test tube from which the clear solution, called supernatant, can be poured out -a process called decantation. The precipitate is resuspended in pure water by stirring with a clean glass rod, centrifuged, and decanted again to wash out any residual impurities. The washed precipitate is used to separate and confirm the group 1 cations and the supernatant is saved for analysis of group 2, 3, 4, and 5 cations.

$$Pb^{2+}(aq) + 2\,Cl^-(aq) \rightleftharpoons PbCl_2(s)\downarrow$$

$$Hg_2^{2+}(aq) + 2\,Cl^-(aq) \rightleftharpoons Hg_2Cl_2(s)\downarrow$$

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)\downarrow$$

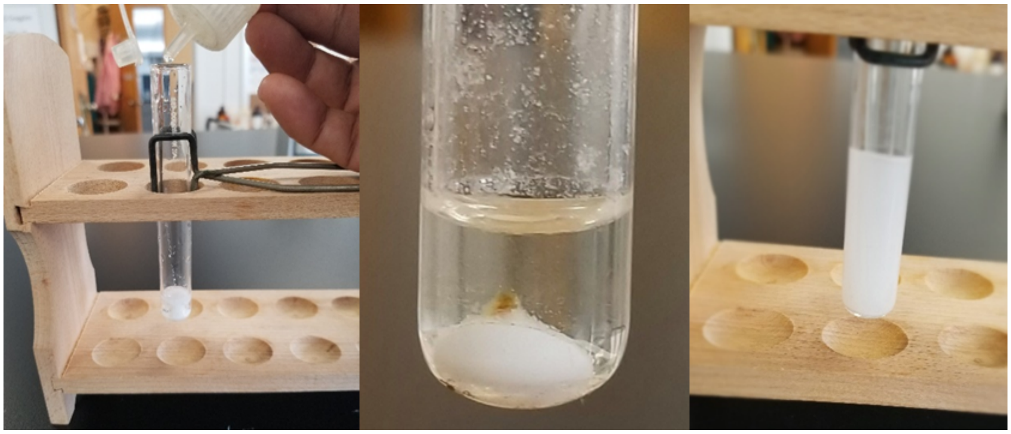


Figure 3.1.1: Precipitates of group I cations formed as a suspension upon addition of HCl drops to the test sample (left), the precipitate separated as a pellet at the bottom of the test tube by centrifugation with a clear supernatant at the top (middle), and the precipitate resuspended in washing liquid (right).

3.2: Separation and confirmation of individual ions in group I precipitates

Separation and confirmation of lead(II) ion

Solubility of $PbCl_2$ in water at 20 ºC is about 1.1 g/100 mL, which is significantly higher than 1.9 x 10^{-4} g/100 mL for $AgCl$ and 3.2 x 10^{-5} g/100 mL for Hg_2Cl_2. Further, the solubility of $PbCl_2$ increases three-fold to about 3.2 g/100 mL in boiling water at 100 ºC, while solubility $AgCl$ and Hg_2Cl_2 remain negligible. A 15 drops sample that is used to precipitate out group I cations corresponds to about 0.75 mL, which based on the molar mass of $PbCl_2$ is 278.1 g and the concentration of each ion ~0.1M, contains about 0.02 g of $PbCl_2$ precipitate. This 0.02 g of $PbCl_2$ requires ~0.6 mL of heated water for dissolution. The precipitated is re-suspended in ~2 mL water and heated in a boiling water bath to selectively dissolve $PbCl_2$, leaving any $AgCl$ and Hg_2Cl_2 almost undissolved, as shown in Figure $3.2.1$.

$$\mathrm{PbCl_2(s)} \overset{Hot\,water}{\rightleftharpoons} \mathrm{Pb^{2+}(aq) + 2\,Cl^-(aq)}$$

The heated suspension is filtered using a heated gravity filtration set up to separate the residue comprising of $AgCl$ and Hg_2Cl_2 from filtrate containing dissolved $PbCl_2$.

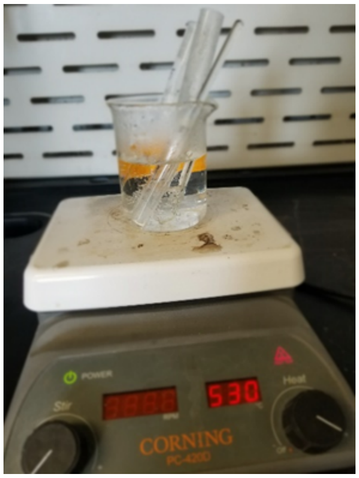


Figure $3.2.1$: Group I precipitate resuspended in water and being heated in a water bath to redissolve $PbCl_2$.

The solubility of $PbCl_2$ is three times less at room temperature than in boiling water. Therefore, the 2 mL filtrate is cooled to room temperature to crystalize out $PbCl_2$:

$$\mathrm{Pb^{2+}(aq) + 2\,Cl^-(aq)} \overset{Cold\,water}{\rightleftharpoons} \mathrm{PbCl_2(s)}$$

If $PbCl_2$ crystals are observed in the filtrate upon cooling to room temperature, it is a confirmation of $PbCl_2$ in the test solution. If $PbCl_2$ concentration is low in the filtrate, the crystals may not form upon cooling. Few drops of 5M HCl are mixed with the filtrate to force the crystal formation based on the **common ion effect** of Cl^- in the reactants. The formation of $PbCl_2$ crystals confirms Pb^{2+} as shown in Figure $3.2.2$, and no crystal formation at this stage confirms that Pb^{2+} was absent in the test solution.

Figure 3.2.2: $PbCl_2$ recrystallized upon cooling the hot solution and addition of two drops of 6M HCl.

Separating mercury(I) ion from silver(I) ion and confirming mercury(I) ion

The residue left after filtering out Pb^{2+} in hot water, is washed further with 10 mL of hot water to washout residual $PbCl_2$. Then 2 mL of 6M aqueous NH_3 solution is passed through the residue drop by drop. Aqueous NH_3 dissolves AgCl precipitate by forming water soluble complex ion $[Ag(NH_3)_2(aq)]^+$ through following series of reactions:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_f = 1.8\times 10^{-10}$$

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \quad K_f = 1.7\times 10^{7}$$

> $$\text{Overall reaction: } AgCl(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq) \quad K = 3.0\times 10^{-3}$$

The 2 mL filtrate is collected in a separate test tube for confirmation of Ag^+ ion. Although Hg_2Cl_2 precipitate is insoluble in water, it does slightly dissociate like all ionic compounds. The Hg_2^{2+} ions undergo auto-oxidation or disproportionation reaction producing black Hg liquid and Hg_2^{2+} ions. The Hg_2^{2+} ions react with NH_3 and Cl^- forming white water-insoluble $HgNH_2Cl$ precipitate through the following series of reactions:

$$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2\,Cl^-(aq)$$

$$Hg_2^{2+}(aq) \rightleftharpoons Hg(l) + Hg^{2+}(aq)$$

$$Hg^{2+}(aq) + 2\,NH_3(aq) + Cl^-(aq) \rightleftharpoons HgNH_2Cl(s) + NH_4^+(aq)$$

> $$\text{Overall reaction: } Hg_2Cl_2(s, \text{white}) + 2\,NH_3(aq) \rightleftharpoons HgNH_2Cl(s, \text{white}) + NH_4^+(aq) + Cl^-(aq) + Hg(l, \text{black})$$

A mixture of white solid $HgNH_2Cl$ and black liquid Hg appears gray in color. Turning of white Hg_2Cl_2 precipitate to grayish color upon addition of 6M NH_3 solution drops confirms Hg_2^{2+} ions are present in the test solution as shown in Figure 3.2.3. If the white precipitate redissolves leaving behind no grayish residue, it means the precipitate was AgCl and Hg_2^{2+} were absent in the test solution.

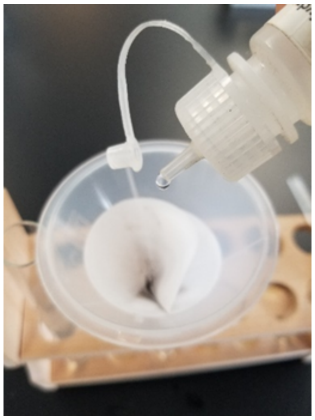


Figure 3.2.3: Confirmation of Hg_2^{2+}, i.e., white precipitates turn grayish-black upon addition of 6M NH_3 solution.

Confirming silver(I) ion

Although water-soluble complex ion $[Ag(NH_3)_2(aq)]^+$ is quite stable, it does slightly decompose into Ag^+ and $NH_3(aq)$. The excess NH_3 added to dissolve $AgCl$ precipitate and the that produced by dissociation of $[Ag(NH_3)_2(aq)]^+$ is removed by making the solution acidic by adding 6M HNO_3. The Cl^- formed from the dissolution of $AgCl$ precipitate in the earlier reactions is still present in the medium. Decomposition of $[Ag(NH_3)_2(aq)]^+$ in the acidic medium produces enough Ag^+ ions to re-form white $AgCl$ precipitate by the following series of equilibrium reactions.

$$[Ag(NH_3)_2]^+(aq) \rightleftharpoons Ag^+(aq) + 2\,NH_3(aq)$$

$$2\,NH_3(aq) + 2\,H_3O^+(aq) \rightleftharpoons 2\,NH_4^+(aq) + 2\,H_2O(l)$$

$$Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s, white)$$

> $$\text{Overall reaction: } [Ag(NH_3)_2]^+(aq) + 2\,H_3O^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s, white) + 2\,NH_4^+(aq) + 2\,H_2O(l)$$

The formation of white $AgCl$ precipitate at this stage in the acidified filtrate confirms Ag^+ ion was present in the test solution, as shown in Figure 3.2.4, and its absence confirms that Ag^+ ion was not present in the test solution.

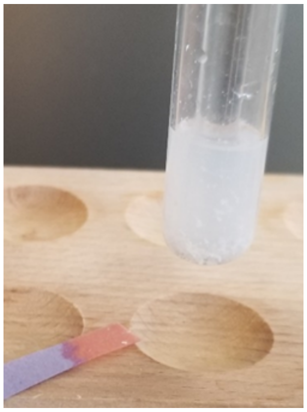


Figure 3.2.4: Confirmation of Ag^+: formation of white precipitate upon converting $[Ag(NH_3)_2(aq)]^+$ solution from alkaline to acidic by addition of HNO_3.

3.3: Procedure, flowchart, and datasheets for separation and confirmation of group I cations

Table 1: List of chemicals and their hazards*

Chemical	Hazard
0.1M Lead(II) nitrate in 0.1M nitric acid	Toxic, irritant, and oxidant
0.1M Mercury(I) nitrate in 0.1M nitric acid	Highly toxic and oxidant
0.1M silver nitrate in 0.1M nitric acid	Toxic, corrosive, and oxidant

- *Hazards of 6M ammonia, 6M hydrochloric acid, and 6M nitric acid are listed in a common reagents table in chapter 2.

Caution

- Used heavy metal ion solutions or precipitates are disposed of in a labeled metal waste disposal container, do not drain these solutions down the drain or in the regular trash.

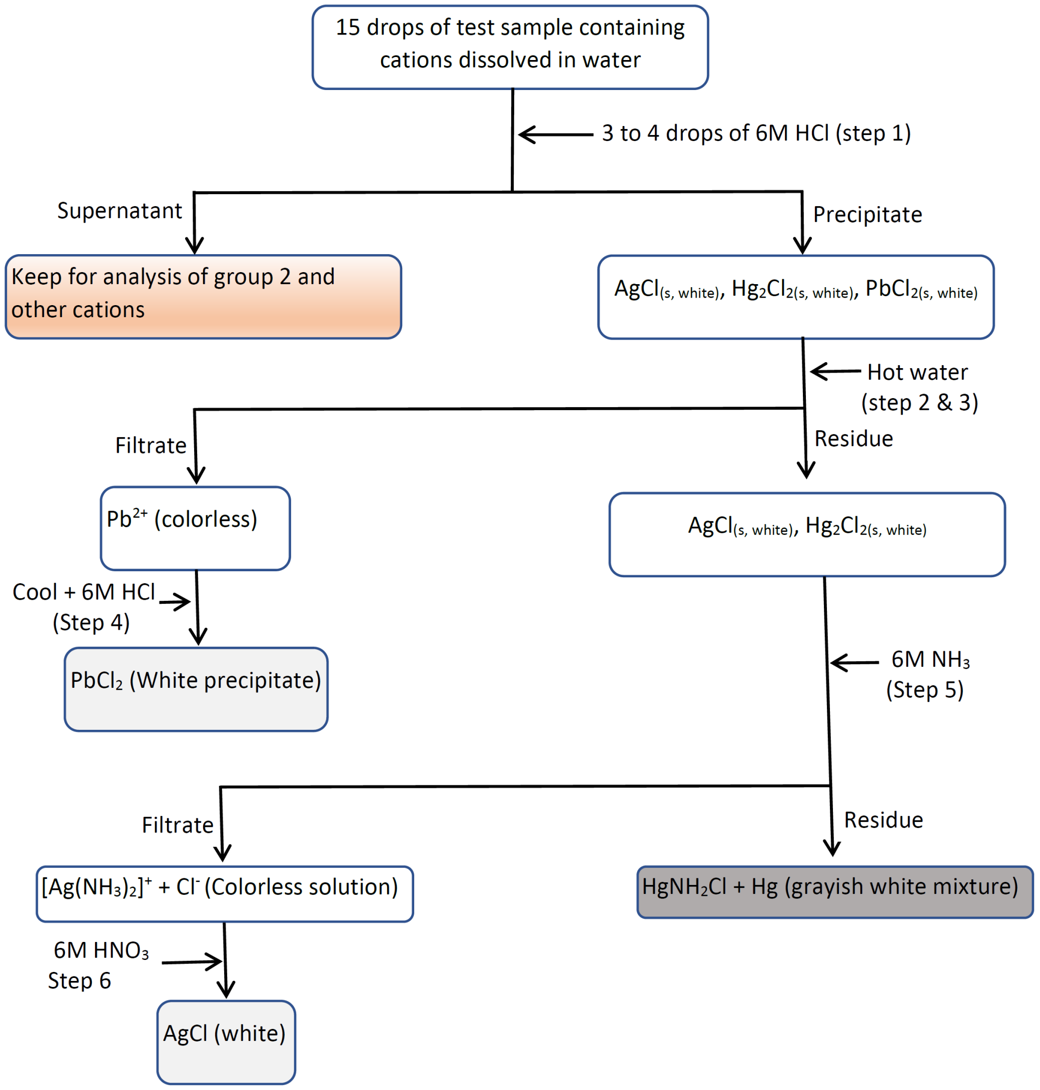
Procedure for the analyses of group I cations

1. Take 15 drops of the unknown solution in a test tube and add 3 to 4 drops of 6M HCl to it drop by drop while stirring. Centrifuge for 2 min and without decanting add 1 more drop of 6M HCl to check there is no more precipitation formation. If more precipitate forms, centrifuge and check again till no more precipitate forms upon addition of a drop 6M HCl to the supernatant. Carefully decant and **keep the supernatant for analysis of group 2 cations**, and **use the precipitate in the next step** for separation and conformation group 1 cation, i.e., $\mathrm{AgCl(s, white)}$, $\mathrm{Hg_2Cl_2(s, white)}$, $\mathrm{PbCl_2(s, white)}$. Record the observations in the datasheet.
2. Add 2 mL (40 drops) of distilled water to the precipitate from step 1 in a test tube, stir it with a clean glass rod to re-suspend the precipitate, and heat the test tube in a boiling water bath for 3 min while stirring. Add 15 mL of distilled water to a 2nd test tube and heat it also in the boiling water bath.
3. Prepare a gravity filtration setup and pass ~5 mL of hot water from the 2nd test tube of step 2 to make it a heated gravity filtration setup. Discard the filtrate which is just hot water. Place an empty test tube labeled "Lead(II) confirmation test" under the heated filter funnel, filter the contents of the first test tube of step 2 and collect it and **keep the filtrate** for $\mathrm{Pb^{2+}}$ test in the test tube labeled "Lead (II) confirmation test". **Keep the residue**, if there is any, for $\mathrm{Ag^{+}}$ and $\mathrm{Hg_2^{2+}}$ tests. If there is no precipitate left, it means $\mathrm{Ag^{+}}$ and $\mathrm{Hg_2^{2+}}$ ions were absent in the test sample.
4. Let the 2 mL filtrate, in the test tube labeled "Lead (II) confirmation test", cool down to room temperature by placing the test tube in a room temperature water bath. If white crystals/precipitate forms in the filtrate upon cooling $\mathrm{Pb^{2+}}$ was present in the test sample. If no crystal forms upon cooling, add 2 to 3 drops of 6M HCl to the filtrate while stirring with a glass rod. If white crystals/precipitate forms $\mathrm{Pb^{2+}}$ was present in the test sample. If no white crystals/precipitate is observed at this stage $\mathrm{Pb^{2+}}$ was absent in the test sample. Discard the mixture in the metal waster container. Record the observation in the datasheet.
5. Re-suspend the residue, if there is any, from step 3 in ~5 mL of hot water from the 2nd test tube of step 2 to dissolve any residual $\mathrm{PbCl_2}$ and then filter it out. Wash the residue with the remaining ~5 mL hot water from the 2nd test tube of step 2. Discard the filtrate which is just the wash liquid with impurities in it and leave the precipitate on the filter paper. Put a clean empty test tube under the filtration funnel and add 40 drops (2 mL) of 6M $\mathrm{NH_3}$ onto the residue drop by drop with genal stirring with a glass rod. **Keep the filtrate** for $\mathrm{Ag^{+}}$ test. If residue is still left on the filter paper and changes color from white to grayish-black $\mathrm{Hg_2^{2+}}$ was present in the test sample, otherwise, $\mathrm{Hg_2^{2+}}$ was absent in the test sample. Discard the gray residue in the metal waste container. Record the observation on the datasheet.
6. Add 6M $\mathrm{HNO_3}$ drop by drop to the 2 mL filtrate from step 5, while stirring and keep testing with blue litmus paper until the solution turns from alkaline to acidic indicated by the change of litmus paper color from blue to red. If white suspension/precipitate is observed at this stage it confirms that $\mathrm{Ag^{+}}$ was present in the test sample, otherwise, $\mathrm{Ag^{+}}$ was not present in the test sample. discard the mixture in the metal waste container. Record the observations in the datasheet.

Datasheets filling instructions for group I cations

1. Step number refers to the corresponding step number in the procedure sub-section.
2. In “the expected chemical reaction and expected observations column”, write an overall net ionic equation of the reaction that will happen if the ion being processed in the step was present, write the expected color change of the solution, the expected precipitate formed and its expected color, etc.
3. In the “the actual observations and conclusion” column write the color change, the precipitate formed and its color, etc. that is actually observed as evidence, and state the specific ion as present or absent.
4. In “the overall conclusion” row write one by one symbol of the ions being tested with a statement “present” or “absent” followed by evidence/s to support your conclusion.

Group-I Cations Analysis Flow Chart



Data sheet for known Group 1 cations (Pb^{2+}, Hg_2^{2+}, and Ag^{1+}) analysis

Students Name: ______________________________ Group partners: ____ Date: ______

Step# **Net ionic equation, and observations from the expected reaction**	**Actual observations and conclusion**
Step 1	
Step 2	
Step 4	
Step 5	
Step 6	
Overall conclusion	

Data sheet for unknown sample number__________ for Group 1 cations (Pb^{2+}, Hg_2^{2+}, and Ag^{1+}) analysis

Students Name: ____________________________ Group partners: ____ Date: ______

Step#	**Net ionic equation, and observations from the expected reaction**	**Actual observations and conclusion**
Step 1		
Step 2		
Step 4		
Step 5		
Step 6		
Overall conclusion		

CHAPTER OVERVIEW

4: Group II cations

4.1: Precipitation of group II cations

The bases of Group II cations separation

The solubility guideline#1 of insoluble ions states “Hydroxide (OH^{-}) and sulfides (S^{2-}) are insoluble except when the cation is alkali metal, ammonia, or a heavy alkaline earth metal ion, i.e., Ca^{2+}, Ba^{2+}, and Sr^{2+}”. The sulfide of Cr^{3+} is also in the exceptions list as its sulfide is unstable in water. It is obvious that the number of insoluble sulfides and hydroxides is large. The solution is made acidic to decrease $[OH^{-}]$ to below the level that can cause precipitation of any ion. The $[S^{2-}]$ also remains low due to the common ion effect of H_3O^{+} in the acidic medium as explained in the next section. Therefore among the insoluble sulfides, only those that have very low solubility limits are selectively precipitated. These include Bi^{3+}, Cd^{2+}, Cu^{2+}, and Sn^{4+} among the cations selected in this study that are left in the solution after group I cations have been separated. Group II comprise of Bi^{3+}, Cd^{2+}, Cu^{2+}, and Sn^{4+}.

Precipitation of group II cations

Among the ions in the initial solution after removal of group I cations, the following ions form insoluble sulfides: Bi^{3+}, Cd^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, and Sn^{4+}. Among these, Bi^{3+}, Cd^{2+}, Cu^{2+}, and Sn^{4+} are in group II that form very insoluble sulfides, and Cr^{3+}, Fe^{2+}, Fe^{3+}, and Ni^{2+} are in group III form insoluble hydroxides and sulfides in basic medium, as reflected by their solubility product constants (K_{sp}) listed in Table 1. The minimum concentration of S^{2-} needed to start precipitation of the cation can be calculated from the K_{sp} expressions as shown in Table 1. It can be observed from Table 1 that there is a huge difference in the minimum S^{2-} concentration (1.8 x 10^{-20}M) needed to precipitate Ni^{2+} -the least soluble sulfide of group III and Cd^{2+} (7.8 x 10^{-26}) -the most soluble sulfide of group II. If the S^{2-} is kept more than 1.8 x 10^{-20} M but less than 7.8 x 10^{-26} M group II cations will selectively precipitate while group III cations and the rest of the cations will remain dissolved.

Table 1: Solubility product constants of insoluble sulfides of group II, and group III and minimum sulfide ion concentration needed to start precipitation from 0.1M cation solution*.

Ion	**Sulfide**	**K_{sp} at 25 ^{o}C**	**Minimum [S^{-2}] needed to precipitate**
Fe^{2+}	FeS	$K_{sp} = [Fe^{2+}][S^{2-}] = 4.9 \times 10^{-18}$	$[S^{-2}] = K_{sp}/[Fe^{2+}] = 4.9 \times 10^{-17}$
Ni^{2+}	NiS	$K_{sp} = [Ni^{2+}][S^{2-}] = 1.8 \times 10^{-21}$	$[S^{-2}] = K_{sp}/[Ni^{2+}] = 1.8 \times 10^{-20}$
Cd^{2+}	NiS	$K_{sp} = [Cd^{2+}][S^{2-}] = 7.8 \times 10^{-27}$	$[S^{-2}] = K_{sp}/[Cd^{2+}] = 7.8 \times 10^{-2}$
Bi^{3+}	Ba_2S_3	$K_{sp} = [Bi^{3+}]^2[S^{2-}]^3 = 6.8 \times 10^{-97}$	$[S^{-2}] = \sqrt[3]{K_{sp}/[Bi^{3+}]^2} = 4.1 \times 10$
Sn^{4+}	SnS_2	$K_{sp} = [Sn^{4+}][S^{2-}]^2 = 1.0 \times 10^{-70}$	$[S^{-2}] = \sqrt[2]{K_{sp}/[Sn^{4+}]} = 3.2 \times 10$
Cu^{2+}	CuS	$K_{sp} = [Cu^{2+}][S^{2-}] = 8.7 \times 10^{-36}$	$[S^{-2}] = K_{sp}/[Fe^{2+}] = 8.7 \times 10^{-35}$

- * Following cations that may be present the initial solution are not listed in this table due to the following reasons: i) group I cations, i.e., Pb^{2+}, Hg_2^{2+}, and Ag^{+} are already removed, ii) Ca^{2+} and Ba^{2+} for soluble sulfides, iii) sulfide of Cr^{3+} is not stable in water, and iv) Fe^{3+} is reduced to Fe^{2+} by H_2S in acidic medium: $2\,Fe^{3+}(aq) + S^{2-} \rightleftharpoons 2\,Fe^{2+}(aq) + S(s)$. Source of K_{sp} values: chem 202 lab manual, 2008, by Michael Stranz, cengag learning, ISBN 13: 978-0-534-66904-1

Source of S^{2-} is H_2S gas -a week diprotic acid that dissociated in water by the following equilibrium reactions:

$$H_2S(g) + H_2O(l) \rightleftharpoons H_3O^{+}(aq) + HS^{-}(aq) \quad K_{a1} = [H_3O^{+}]\,[HS^{-}]\,/\,[H_2S] = 1.0 \times 10^{-7}$$

$$HS^{-}(aq) + H_2O(l) \rightleftharpoons H_3O^{+}(aq) + S^{2-}(aq) \quad K_{a2} = [H_3O^{+}]\,[S^{2-}]\,/\,[HS^{-}] = 1.3 \times 10^{-13}$$

> Overall reaction: $H_2S(g) + 2\,H_2O(l) \rightleftharpoons 2\,H_3O^{+}(aq) + S^{2-}(aq) \quad K_a = [H_3O^{+}]^2\,[S^{2-}]\,/\,[H_2S] = 1.3 \times 10^{-20}$

Extent of H_2S dissociation, and, consequently, the concentration of S^{2-} produced is dependent on H_3O^{+}:

$$K_a = \frac{[H_3O^{+}]^2[S^{2-}]}{[H_2S]} \qquad \text{rearranges to:} \qquad [S^{2-}] = \frac{K_a[H_2S]}{[H_3O^{+}]^2}$$

It is obvious from the above formula that $[\mathrm{S}^{2-}]$ is dependent on $[\mathrm{H_3O^+}]$, which is related to pH ($pH = Log\frac{1}{[\mathrm{H_3O^+}]}$ = -Log$[\mathrm{H_3O^+}]$. Therefore, $[\mathrm{S}^{2-}]$ can be controlled by adjusting the pH.

H_2S is a toxic gas. To minimize the exposure, H_2S is produced in-situ by decomposition of thioacetamide ($\mathrm{CH_3CSNH_2}$) in water:

$$\mathrm{CH_3CSNH_2(aq) + 2\,H_2O \rightleftharpoons CH_3COO^- + NH_4^+(aq) + H_2S(aq)}$$

The decomposition of thioacetamide is an endothermic reaction, which, according to Le Chatelier's principle, moves in the forward direction upon heating. An aqueous solution of thioacetamide is heated in a boiling water bath in a fume hood producing ~0.01M H_2S solution.

Rearranging acid dissociation constant of H_2S and plugging in 0.01M H_2S in the rearranged formula allows calculating S^{2-} concentration at various concentrations of $\mathrm{H_3O^+}$, i.e., at various pH values:

$$[\mathrm{S}^{2-}] = \frac{K_a[\mathrm{H_2S}]}{[\mathrm{H_3O^+}]^2} = \frac{1.3\times10^{-20}\times0.01}{[\mathrm{H_3O^+}]^2} = \frac{1.3\times10^{-22}}{[\mathrm{H_3O^+}]^2}$$

It shows that S^{2-} concentration can be varied by $[\mathrm{H_3O^+}]$, i.e., by varying pH. At pH 1 and 0, $\mathrm{H_3O^+}$ is 0.10 M and 1.0 M, respectively, that produces $[\mathrm{S}^{2-}]$ in the range of 1.3 x 10^{-20} M S^{2-} and 1.3 x 10^{-22} M S^{2-}:

$$[\mathrm{S}^{2-}] = \frac{1.3\times10^{-22}}{(0.10)^2} = 1.3\times10^{-20}\ M \qquad \text{and} \qquad [\mathrm{S}^{2-}] = \frac{1.3\times10^{-22}}{(1.0)^2} = 1.3\times10^{-22}\ M$$

This range of $[\mathrm{S}^{2-}]$ is less than the solubility limit of Ni^{2+} -the least soluble cation of group III but more than the solubility limit of Cd^{2+} -the most soluble cation of group II. If pH of the test solution is maintained between 0 and 1, group II cations will precipitate and group III and higher group cations will remain dissolved. At pH 0.5, S^{2-} is 5.2 x 10^{-22} M that will precipitate more than 99.99% Cd^{2+}:

$$\mathrm{K_{sp}} = \left[\mathrm{Cd}^{2+}\right]\left[\mathrm{S}^{2-}\right] = 7.8\times10^{-27} \qquad \text{gives:} \qquad [\mathrm{Cd}^{2+}] = \frac{7.8\times10^{-27}}{[\mathrm{S}^{-2}]} = \frac{7.8\times10^{-27}}{5.2\times10^{-22}} = 1.5\times10^{-5}\ M$$

, which is 0.0002% of the initial $[\mathrm{Cd}^{2+}]$.

The supernatant after removal of group I chlorides is usually within the pH range of 0.5 ±0.3, which is the appropriate pH for precipitation of group II cations under the conditions of this study. If the pH of the test sample is outside this range, the pH can be increased to ~0.5 by adding 0.5M $\mathrm{NH_3(aq)}$ drop by drop under stirring. Determine pH by using a pH paper after each drop of 0.5M $\mathrm{NH_3(aq)}$ is added and thoroughly mixed. Keep in mind that $\mathrm{NH_3}$ solution in water is also labeled as $\mathrm{NH_4OH}$. Similarly, the pH can be decreased to ~0.5 by adding 0.5M $\mathrm{HCl(aq)}$ drop by drop under stirring. Determine pH by using a pH paper after each drop of 0.5M $\mathrm{HCl(aq)}$ is added and thoroughly mixed.

> Thioacetamide reagent is added to the test solution at pH ~0.5 and heated in a boiling water bath to precipitate out group II cations.

The precipitates include $\mathrm{SnS_2}$ (yellow), CdS (yellow-orange), CuS (Black-brown), $\mathrm{Bi_2S_3}$ (black), formed by the following precipitation reactions:

$$\mathrm{SnCl_6^{2-}(aq) + 2\,S^{2-}(aq) \rightleftharpoons 6\,Cl^-(aq) + SnS_2(s, yellow)}$$

$$\mathrm{Cd^{2+}(aq) + S^{2-}(aq) \rightleftharpoons CdS(s, yellow-orange)}$$

$$\mathrm{Cu^{2+}(aq) + S^{2-}(aq) \rightleftharpoons CuS(s, black-brown)}$$

$$\mathrm{2\,Bi^{3+}(aq) + 3\,S^{2-}(aq) \rightleftharpoons Bi_2S_3(s, black)}$$

The overall color of the combined precipitate may vary depending on its composition. Black color dominates, i.e., if all precipitates are present, the color of the mixture will be black as shown in Figure 4.1.1.

Figure 4.1.1: Mixture of Group II precipitates, i.e., SnS_2 (yellow), CdS (yellow-orange), CuS (Black-brown), and Bi_2S_3 (black).

The solution is cooled to room temperature by using a room temperature water bath. Cooling helps precipitation of CdS. A drop of 0.5 M $NH_3(aq)$ is added while stirring, which promotes precipitation of CdS and CnS_2, as both tend to stay dissolved in a supersaturated solution. The mixture is centrifuged and decanted to separate the supernatant that is used for the analysis of group III and higher group cations. The precipitate is washed with 0.1M NH_4Cl solution and the washed precipitate is used to separate and confirm individual cations of group II.

4.2: Separation and confirmation of individual ions in group II precipitates

Separation and confirmation of tin(IV) ion

Among the sulfides of group II, only $\mathrm{SnS_2}$ is amphoteric and reacts with $\mathrm{OH^-}$ ions in an alkaline medium to produce $[\mathrm{Sn(OH)_6}]^{2-}$ -a coordination complex anion, and stannate ion $[\mathrm{SnS_3}]^{2-}$, both are water-soluble. 3M KOH is mixed with the precipitates of group II ions and the mixture is heated to dissolve the $\mathrm{SnS_2}$ through the following equilibrium reaction:

$$3\,\mathrm{SnS_2(s, yellow)} + 6\,\mathrm{OH^-(aq)} \rightleftharpoons [\mathrm{Sn(OH)_6}]^{2-}\mathrm{(aq)} + 2\,[\mathrm{SnS_3}]^{2-}\mathrm{(aq)}$$

The hot solution is centrifuged and decanted to separate the supernatant that contains $[\mathrm{Sn(OH)_6}]^{2-}$ and $[\mathrm{SnS_3}]^{2-}$ dissolved in it and the precipitate that contains the sulfides of the rest of the group II cations, as shown in Figure 4.2.1. A better approach is to separate the supernatant by aspiration using the cotton-plug technique to avoid contamination of precipitates in the supernatant.

Figure 4.2.1: Supernatant containing $[\mathrm{Sn(OH)_6}]^{2-}$ and $[\mathrm{SnS_3}]^{2-}$ (left test tube) and blackish precipitate (right test tube) containing mixture of CdS (yellow-orange), CuS (Black-brown), and $\mathrm{Bi_2S_3}$ (black).

The above reaction is reversible, which means removing $\mathrm{OH^-}$ from the supernatant by acid-base neutralization reaction moves the equilibrium in the reverse direction re-producing yellow $\mathrm{SnS_2}$ precipitate as shown in Figure 4.2.2.

$$[\mathrm{Sn(OH)_6}]^{2-}\mathrm{(aq)} + 2\,[\mathrm{SnS_3}]^{2-}\mathrm{(aq)} \rightleftharpoons 3\,\mathrm{SnS_2(s, yellow)} + 6\,\mathrm{OH^-(aq)}$$

$$6\,\mathrm{HCl(aq)} + 6\,\mathrm{OH^-(aq)} \rightleftharpoons 6\,\mathrm{H_2O(l)} + 6\,\mathrm{Cl^-(aq)}$$

$$\text{Overall reaction: } 6\,\mathrm{HCl(aq)} + [\mathrm{Sn(OH)_6}]^{2-}\mathrm{(aq)} + 2\,[\mathrm{SnS_3}]^{2-}\mathrm{(aq)} \rightleftharpoons 3\,\mathrm{SnS_2(s, yellow)} + 6\,\mathrm{H_2O(l)}$$

Figure 4.2.2: $\mathrm{Sn^{4+}}$ yellow precipitate confirming the presentence of $\mathrm{Sn^{4+}}$ in the test sample.

Some of the sulfides may be lost due to air oxidation of $\mathrm{H_2S}$ by the following reaction:

$$2\,\mathrm{H_2S(aq)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{S(s, whitish{-}yellow)} + 2\,\mathrm{H_2O(l)}$$

To compensate for the loss of sulfide, 1M thioacetamide solution is also added along with 6M HCl to the supernatant and the mixture is heated to reform the yellow $\mathrm{SnS_2}$ precipitate that confirms the presence of $\mathrm{Sn^{4+}}$ in the test solution. Note that both S and SnS_2 are yellow solids. Add 3M KOH solution to the mixture to turn it alkaline again the SnS_2 precipitate will re-dissolve confirming Sn^{4+} is present in the test solution. The S particles will not re-dissolve.

Separation and confirmation of cadmium(II) ion

CdS is the most soluble sulfide among group II sulfide precipitates. According to Le Chatelier's principle, the removal of products, i.e., Cd^{2+} and S^{2-} of the dissolution reaction in this case, drives the reaction forward. CdS can be redissolved by adding 1M HCl to the precipitates after the removal of Sn^{4+}. Dissociation of HCl produces H_3O^+ in water that removes S^{2-} by forming H_2S which is a weak acid. At the same time, Cl^- removes Cd^{2+} b y forming soluble coordination complex anion $[CdCl_4]^{2-}$ which is quite stable with $K_f = 6.3\times10^2$:

$$\mathrm{CdS(s, yellow-orange) \rightleftharpoons Cd^{2+}(aq) + S^{2-}(aq)}$$

$$\mathrm{4\,HCl(aq) + 4\,H_2O(l) \rightleftharpoons 4\,H_3O^+(aq) + 4\,Cl^-(aq)}$$

$$\mathrm{S^{2-}(aq) + 2\,H_3O^+(aq) \rightleftharpoons H_2S(aq) + 2\,H_2O(l)}$$

$$\mathrm{Cd^{2+}(aq) + 4\,Cl^-(aq) \rightleftharpoons [CdCl_4]^{2-}(aq)}$$

> $$\mathrm{Overall\ reaction:\ CdS(s, yellow-orange) + 4\,HCl(aq) + 2\,H_2O(l) \rightleftharpoons [CdCl_4]^{2-}(aq) + 2\,H_3O^+(aq) + H_2S(aq)}$$

The dissolution of CdSis facilitated by heating the reaction mixture. The rest of the group II cations, i.e., CuS and Bi_2S_3 are very insoluble and do not dissolve under these conditions. The solution is centrifuged and decanted or aspirated to separate the supernatant that contains $[CdCl_4]^{2-}$ and the precipitate that contains CuS and/or Bi_2S_3 if Cu^{2+} and/or Bi^{3+} are present. The precipitate tends to go into the supernatant, so, the cotton plug technique is needed to prevent precipitates from going into the supernatant during the separation as shown in Figure 4.2.3.

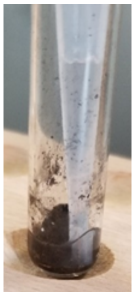


Figure 4.2.3: Clean supernatant containing $[CdCl_4]^{2-}$ being aspirated in the presence of loosely packed CuS and Bi_2S_3 precipitate using cotton-plug at the mouth of pasture pipette.

All the reactions responsible for the dissolution of CdS are reversible. The addition of HCl dissolves CdS by moving the equilibrium forward and the removal of HCl moves the equilibrium in the reverse direction to reform yellow CdS precipitate. Ammonia NH_3 is such a base that removes HCl:

$$\mathrm{HCl(aq) + NH_3(aq) \rightleftharpoons NH_4Cl(aq)}$$

6M NH_3 solution is added drop by drop under stirring and tested with red-litmus paper till the solution turns alkaline. If yellow precipitate forms, it is CdS confirming Cd^{2+} was present in the test solution:

$$\mathrm{[CdCl_4]^{2-} + 2\,H_3O^+ + H_2S(aq) + 4\,NH_3(aq) \rightleftharpoons CdS(s, yellow-orange)\downarrow + 4\,NH_4^+(aq) + Cl^- + 2\,H_2O(l)}$$

If no precipitate forms, add 1M thioacetamide and heat to make up for any loss of S^{2-} in the solution. If yellow precipitate forms, it is CdS confirming Cd^{2+} is present in the test solution as shown in Figure 4.2.4.

Figure 4.2.4: Yellow precipitate CdS confirming the presence of Cd^{2+} in the test sample.

Separation and confirmation of copper(II) ion and bismuth(III) ion

After removal of Sn^{4+} and Cd^{2+}, if there is a precipitate left it could be CuS and/or Bi_2S_3, which are the least soluble sulfides in group II. To dissolve CuS and Bi_2S_3, the S^{2-} in the products need to be removed to a higher extent than in the case of CdS re-dissolution.

> Nitric acid provides NO_3^{2-} which is a strong oxidizing agent that can remove S^{2-} sufficient to drive the equilibrium forward to dissolve CuS and Bi_2S_3.

$$\mathrm{Bi_2S_3(s,\ black)} \rightleftharpoons \mathrm{2\,Bi^{3+}(aq) + 3\,S^{2-}(aq)}$$

$$\mathrm{3\,S^{2-}(aq) + 2\,NO_3^{-}(aq) + 8\,H_3O^{+}(aq)} \rightleftharpoons \mathrm{3\,S(s,\ yellow)\downarrow + 2\,NO(g)\uparrow + 12\,H_2O(l)}$$

> Overall reaction: $\mathrm{Bi_2S_3(s,\ black) + 2\,NO_3^{-}(aq) + 8\,H_3O^{+}(aq)} \rightleftharpoons \mathrm{3\,S(s,\ yellow)\downarrow + 2\,Bi^{3+}(aq) + 2\,NO(g)\uparrow + 12\,H_2O(l)}$

$$\mathrm{3\,CuS(s,\ black{-}brown)} \rightleftharpoons \mathrm{3\,Cu^{2+}(aq) + 3\,S^{2-}(aq)}$$

$$\mathrm{3\,S^{2-}(aq) + 2\,NO_3^{-}(aq) + 8\,H_3O^{+}(aq)} \rightleftharpoons \mathrm{3\,S(s,\ yellow)\downarrow + 2\,NO(g)\uparrow + 12\,H_2O(l)}$$

> Overall reaction: $\mathrm{3\,CuS(s,\ black{-}brown) + 2\,NO_3^{-}(aq) + 8\,H_3O^{+}(aq)} \rightleftharpoons \mathrm{3\,S(s,\ yellow)\downarrow + 2\,Cu^{2+}(aq) + 2\,NO(g)\uparrow + 12\,H_2O(l)}$

The mixture is heated to enhance the above reactions. The S^{2-} is oxidized to solid light-yellow colored sulfur particles. Brown colored fumes are observed over the solution as a result of air oxidation of nitric oxide (NO) that evaporates out of the solution as shown in Figure 4.2.5:

$$\mathrm{2\,NO(g) + O_2(g)} \rightleftharpoons \mathrm{2\,NO_2(g,\ red{-}brown)}$$

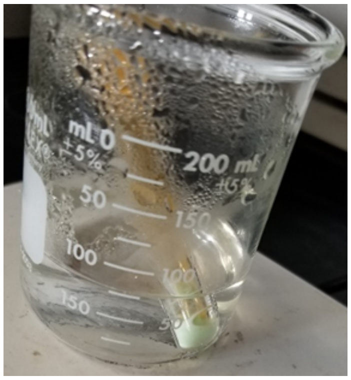


Figure 4.2.5: Yellow sulfur precipitate suspended in the liquid mixture and brown NO_2 gas above the liquid mixture when CuS and Bi_2S_3 precipitate is heated with nitric acid.

> Removal of NO and S^{2-} from the products drives the reaction in the forward direction based on Le Chatelier's principle.

The solid sulfur precipitate is removed by centrifugation followed by decantation.

The supernatant is acidic and appears light blue if copper ions are present, as shown in Figure $4.2.6$.

Figure $4.2.6$: Mixture of copper and bismuth ions in the supernatant after removal of the sulfur precipitate.

> If the solution is made alkaline, Cu^{2+}, and Bi^{3+} form solid hydroxides. However, aqueous ammonia (NH_3) selectively precipitate out $Bi(OH)_3$, while keeping copper dissolved as coordination complex ions, $[Cu(NH_3)_4]^{2+}$:

$$\mathrm{Bi^{3+}(aq) + 3\,NH_3(aq) + 3\,H_2O(l) \rightleftharpoons Bi(OH)_3(s, white)\downarrow + 3\,NH_4^+(aq)} \quad K = 3.3\times 10^{39}$$

$$\mathrm{Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq, blue)} \quad K = 3.8\times 10^{12}$$

The solution is made alkaline by adding 6M NH_3 drop by drop and tested using red-litmus paper. Excess NH_3 solution is added to make sure that any residual Cd^{2+} is also removed as $[Cu(NH_3)_4]^{2+}$. If the supernatant turns blue by making it alkaline with ammonia, it confirms Cu^{2+} is present in the test sample, as shown in Figure $4.2.7$. The presence of residual Cd^{2+} does not interfere because it forms a colorless $[Cu(NH_3)_4]^{2+}$ ion.

Figure $4.2.7$: Confirmation test of copper, i.e., the solution turned dark blue due to $[Cu(NH_3)_4]^{2+}$ ions upon turning alkaline with ammonia. The solution is turbid due to $Bi(OH)_3$ precipitate (left), and becomes clear after removal of $Bi(OH)_3$ by centrifugation (right).

The mixture is centrifuged and decanted to separate the white precipitate of $Bi(OH)_3$, but, if ammonia addition was not sufficient, white $Cd(OH)_2$ may also form from any residual Cd^{2+} ions:

$$\mathrm{Cd^{2+}(aq) + 2\,NH_3(aq) + 2\,H_2O(l) \rightleftharpoons Cd(OH)_2(s, white)\downarrow + 2\,NH_4^+}$$

The precipitate is resuspended in 6M NH_3 to redissolve $Cd(OH)_2$, if there is any present. $Bi(OH)_3$ precipitate does not dissolve in 6M NH_3. If the white precipitate persists after washing with 6M NH_3 it confirms Bi^{3+} is present in the test solution, as shown in Figure $4.2.8$.

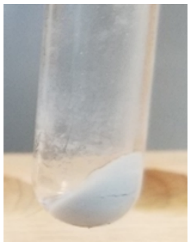


Figure 4.2.8: $Bi(OH)_3$ precipitate after washing with 6M NH_3, confirming the presence of Bi^{3+} in the test sample.

4.3: Procedure, flowchart, and datasheets for separation and confirmation of group II cations

Table 1: List of chemicals and their hazards*

Chemical	**Hazard**
0.1M ammonium chloride (NH_4Cl)	Toxic and irritant
0.1M bismuth nitrate in 0.3M HNO_3	Toxic, irritant, and oxidant
0.1M cadmium chloride in 0.3M HNO_3	Toxic and suspected carcinogen
0.1M copper(II) nitrate in 0.3M HNO_3	Toxic, irritant, and oxidant
0.1M Tin(IV) chloride in 0.3M HNO_3	Corrosive and irritant

- *Hazards of 6M ammonia, 6M hydrochloric acid, 6M nitric acid, 3M potassium hydroxide, and 1M thioacetamide are listed in the common reagents table in chapter 2.

Caution

- Used heavy metal ion solutions or precipitates are disposed of in a labeled metal waste disposal container, do not drain these solutions down the drain or in the regular trash.

Procedure for the analyses of group II cations

1. Take 15 drops of the test solution if the group I cations are not present in the sample or take the **supernatant of step 1 of group I analysis**. Find its pH using a short-range pH paper. If the pH is 0.5 ±3 there is no need to adjust the pH. If pH is lower, increase it to 0.5 ±3 by adding drops of 0.5M ammonia solution, one drop at a time while stirring. If pH is higher, decrease to 0.5 ±3 by adding drops of 0.5M HCl, one drop at a time while stirring. Then add 10 drops of 1M thioacetamide stir and heat for 10 min in a water bath. Add 1 drop of 0.5M NH_3,stir, centrifuge for 2 min, and add 5 drops of 1M thioacetamide, stir, and heat again for 2 min. Cool in room temperature water bath and add 1 more drop of 0.5M ammonia while stirring and centrifuge for 2 min. Decant and **keep the supernatant** for group III cations and **keep the precipitate** for separation and analysis of group II cations. The precipitate may be one or more of the following: SnS_2 (yellow), CdS (yellow-orange), CuS (black-brown), Bi_2S_3 (black). Record the observation in the datasheet.
2. Wash the precipitate from step 1 by re-suspending it in 1 mL (20 drops) of 0.1M NH_4Cl, centrifuge for 2 min, decant, and discard the supernatant which is just the washing liquid. Re-suspend the precipitate in 1 mL (20 drops) of 3M KOH + 1 drop of 1M thioacetamide, stir, loosely stopper the test tube, and heat in a water bath for 2 min. Centrifuge the hot mixture for 2 min and decant while it is hot. **Keep the supernatant** for analysis of Sn^{4+} which exists as soluble $Sn(OH)_6^{2-}$ ion at this stage and **keep the precipitate**, if there is any, for analysis of the rest of the group II cations. Record the observation in the datasheet.
3. Add 6M HCl drop by drop to the supernatant from step 2 and keep testing with blue litmus paper until the mixture turns acidic. Then add 5 drops of 1M thioacetamide, stir, and heat in a water bath for 2 min. Yellow precipitate at this stage is SnS_2 which confirms Sn^{4+} is present in the test sample, no yellow precipitate means Sn^{4+} was not present. Record the observation in the datasheet and discard the mixture in a waste container.
4. Wash the precipitate from step 2 by re-suspending it in 10 drops of distilled water and then centrifuge for 2 min. Decant and discard the supernatant and wash the precipitate again by re-suspension in 10 drops of distilled water followed by centrifuge for 2 min, decant and discard the supernatant. Re-suspend the precipitate in 10 drops of distilled water + 2 drops of 6M HCl and heat for 2 min. Centrifuge and decant while the mixture is still hot. If the supernatant appears turbid due to some precipitate left in it, use the cotton plug technique to aspire clean supernatant and filter out the residual precipitate. **Keep the supernatant** for analysis of Cd^{2+} which may exist as dissolved $[CdCl_4]^{2-}$ ion at this stage and **keep the precipitate**, if there is any, for analysis of remaining group II cations. Record the observation in the datasheet.
5. Add 6M NH_3 drop by drop to the clear supernatant from step 4 and keep testing with red litmus paper until the solution turns basic. Add 2 drops of 1M thioacetamide, stir, and heat for 2 min in a water bath. If a yellow precipitate forms at this stage it is CdS that confirms Cd^{2+} was present in the test sample, otherwise Cd^{2+} was not present. Record the

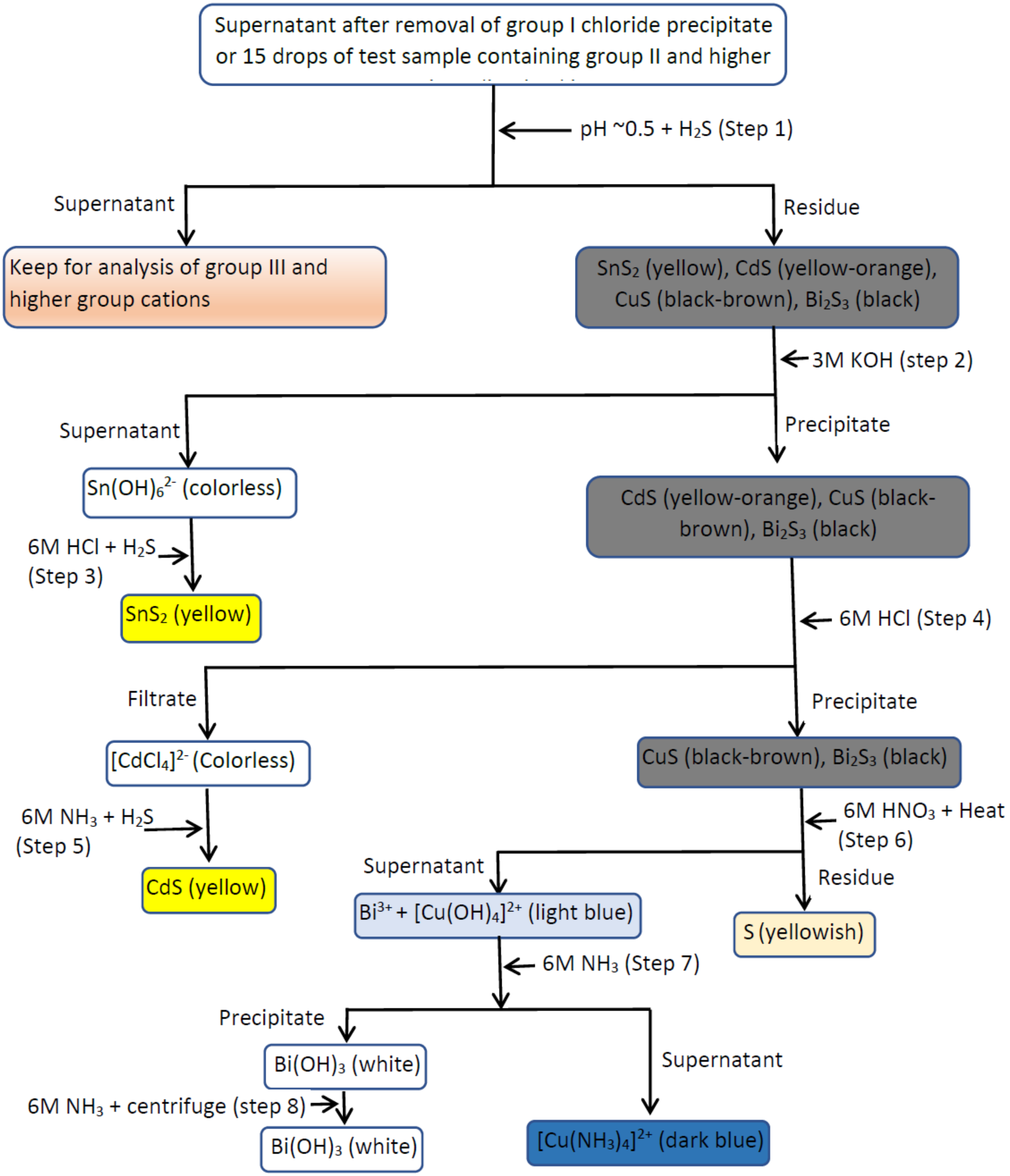
observation in the datasheet and discard the mixture in a metal waste container.

6. Wash the precipitate from step 4, if there is any, by re-suspending it in 10 drops of distilled water, centrifuge for 2 min, decant and discard the supernatant. Re-suspend the precipitate in 10 drops of 6M HNO_3 and heat in a boiling water bath for 5 min. The precipitate, i.e., CuS and/or Bi_2S_3 will dissolve in the liquid, and Cu^{2+} and/or Bi^{3+} hydrated ions and yellow sulfur particles may form. Remove the sulfur particles by centrifugation and decantation and discard them as there is no ion in them. **Keep the supernatant** for the analysis of Cu^{2+} and Bi^{3+} and record the observation in the datasheet.
7. Add 6M NH_3 drop by drop to the supernatant from step 6 and keep testing with red litmus paper till the solution turns alkaline. Add 10 more drops of 6M NH_3 solution after the solution turns alkaline to make it strongly alkaline. If the mixture becomes blue color at this stage, it is due to the blue $[Cu(NH_3)_4]^{2+}$ ion that confirms Cu^{2+} is present in the test solution. If there is a white suspension in the mixture, keep it for testing Bi^{3+}. Record the observation in the datasheet.
8. Centrifuge the mixture from step 7 for 2 min and decant and discard the supernatant. If there is any white precipitate left after decantation, it is most likely $Bi(OH)_3$. Wash the precipitate by re-suspending it in 10 drops of 6M NH_3, centrifuge for 2 min, and decant. If the white precipitate remains there after the washing, it is $Bi(OH)_3$ that confirms Bi^{3+} is present in the test solution, otherwise, Bi^{3+} is absent. Discard the mixture in a metal waste container and record the observation in the datasheet.

Datasheets filling instructions for group II cations

1. Step number refers to the corresponding step number in the procedure sub-section.
2. In “the expected chemical reaction and expected observations column”, write an overall net ionic equation of the reaction that will happen if the ion being processed in the step was present, write the expected color change of the solution, the expected precipitate formed and its expected color, etc.
3. In “the actual observations and conclusion” column write the color change, the precipitate formed and its color, etc. that is actually observed as evidence, and state the specific ion as present or absent.
4. In “the overall conclusion” row write one by one symbol of the ions being tested with a statement “present” or “absent” followed by evidence/s to support your conclusion.

Group-II Cations Analysis Flow Chart



Data sheet for known Group II cations (Sn^{4+}, Cd^{2+}, Cu^{2+}, and Bi^{3+}) analysis

Students Name: ______________________________ Group partners: ______________________________ Date: ______

Step# **Net ionic equation, and observations from the expected reaction**	**Actual observations and conclusion**
Step 1	
Step 2	
Step 3	
Step 4	
Step 5	
Step 6	
Step 7	
Step 8	
Overall conclusion	

Datasheet for unknown sample#_______ of Group II cations (Sn^{4+}, Cd^{2+}, Cu^{2+}, and Bi^{3+}) analysis

Students Name: ___________________________ Group partners: ____ Date: ______

Step#	Net ionic equation, and observations from the expected reaction	Actual observations and conclusion
Step 1		
Step 2		
Step 3		
Step 4		
Step 5		
Step 6		
Step 7		
Step 8		
Overall conclusion		

CHAPTER OVERVIEW

5: Group III cations

5.1: Separation of group III cations

Group II cations form sulfides that have very low solubility. After group II cations are removed under a low concentration of S^{2-} in an acidic medium, the solution is made alkaline. Remember that like sulfides, hydroxides are also insoluble according to insoluble ions rule#1 of solubility guidelines described in chapter 1 states “Hydroxide (OH^-) and sulfides (S^{2-}) are insoluble except when the cation is a heavy alkaline earth metal ion: Ca^{2+}, Ba^{2+}, and Sr^{2+}, alkali metal ions, and ammonium ion.”

Table 1 lists solubility product constants of hydroxides of group III & IV cations at 25 °C, maximum hydroxide (OH^-) concentration, and the maximum pH that can exist in a saturated solution containing 0.1M cation solutions that may be present in the test solution at this stage. It can be observed that the ions listed in table 1 will not precipitate as hydroxides during the precipitation of group II cations under the acidic pH range of 0.5 to 1.

> Fe^{3+} forms the most insoluble hydroxide, but it is reduced to Fe^{2+} by H_2S during precipitation of group II cations:
>
> $$2\,Fe^{3+}(aq) + S^{2-}(aq) \rightleftharpoons 2\,Fe^{2+}(aq) + S(s)$$
>
> Fe^{3+} may be present only if precipitation of group III starts from a fresh sample that has not been subjected to group II separation.

It can be observed from Table 1 that if the pH of the sample solution is increased to a range of 7 to 10, Fe^{3+}, Cr^{3+}, Ni^{2+}, and Fe^{2+} will precipitate as $Fe(OH)_3(s, rusty)$, $Cr(OH)_3(s, gray-green)$, $Ni(OH)_2(s, green)$, and $Fe(OH)_2(s, green)$, leaving behind in the solution rest of the ions that may still be present at this stage. Group III comprise of , Fe^{3+}, Cr^{3+}, Ni^{2+}, and Fe^{2+} ions.

Table 1: Solubility product constants of hydroxides of group III & IV cations at 25 °C, maximum hydroxide (OH^-) concentration, and pH that can exist in a saturated 0.1M cation solution.*

Ion	**Salt**	**K_{sp} at 25 °C**	**Minimum [OH⁻] and pH needed to precipitate**
Fe^{3+}	$Fe(OH)_3$	$K_{sp} = [Fe^{3+}][OH^-]^3 = 2.8 \times 10^{-39}$	$[OH^-] = 3.0 \times 10^{-13}\ M = pH\ 1.5$
Cr^{3+}	$Cr(OH)_3$	$K_{sp} = [Cr^{3+}][OH^-]^3 = 1.0 \times 10^{-30}$	$[OH^-] = 2.2 \times 10^{-10}\ M = pH\ 4.3$
Ni^{2+}	$Ni(OH)_2$	$K_{sp} = [Ni^{2+}][OH^-]^2 = 5.5 \times 10^{-16}$	$[OH^-] == 7.4 \times 10^{-9}\ M = pH\ 4.$
Fe^{2+}	$Fe(OH)_2$	$K_{sp} = [Fe^{2+}][OH^-]^2 = 4.9 \times 10^{-17}$	$[OH^-] = 2.2 \times 10^{-9}\ M = pH\ 5.6$
Ca^{2+}	$Ca(OH)_2$	$K_{sp} = [Ca^{2+}][OH^-]^2 = 5.0 \times 10^{-6}$	$[OH^-] = 7.1 \times 10^{-4}\ M = pH\ 10.$
Ba^{2+}	$Ba(OH)_2$	$K_{sp} = [Ba^{2+}][OH^-]^2 = 2.6 \times 10^{-4}$	$[OH^-] = 5.1 \times 10^{-3}\ M = pH 11.7$

- * Following cations that may be present in the initial solution are not listed in this table due to the reason: i) Pb^{2+}, Hg_2^{2+}, and Ag^+ are already removed as chloride precipitates of group I cations, ii) Sn^{4+}, Cd^{2+}, Cu^{2+}, and Bi^{3+} has been removed as group II sulfides under pH 0.5 to 1, iii) Na^+ and K^+ form soluble compounds with all anions according to rule#1 of solubility described in chapter 1. Source: Engineering ToolBox, (2017). Solubility product constants. [online] Available at: https://www.engineeringtoolbox.com/s...sp-d_1952.html [Accessed Feb. 5th, 2022]

Buffers, that resist change in pH are employed in such a situation where pH needs to be maintained in a narrow range. Buffers are a mixture of a weak acid and its conjugate base or a mixture of a weak base and its conjugate acid. Ammonia (NH_3), i.e., a week base and ammonium ion (NH_4^+) is its conjugate acid.

> The NH_3/NH_4^+ is a suitable buffer that can maintain pH of around 9. The buffer is prepared by adding 2 drops of 6M HCl into 15 drops of the sample and then adding 6M NH_3 drop by drop to neutralize the acid.
>
> $$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
>
> $$NH_3(aq) + H_3O^+(aq) \longrightarrow NH_4^+(aq) + H_2O(l)$$
>
> $$\text{Overall reaction: } HCl(aq) + NH_3(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

> Then 5 drops more of 6M NH_3 are added after the HCl has been neutralized to make a mixture of NH_3 and NH_4^+ that maintains pH ~9 and OH- at around 1 x 10^{-5} M.

The group III cations precipitate at this stage as hydroxides, as shown in Figure 5.1.1, except Ni^{2+}:

$$\begin{gathered}\mathrm{Fe^{3+}(aq) + 3\,OH^-(aq) \longrightarrow Fe(OH)_3(s, reddish{-}brown\ or\ rusty)\downarrow},\\ \mathrm{Cr^{3+}(aq) + 3\,OH^-(aq) \longrightarrow Cr(OH)_3(s, gray{-}green)\downarrow},\\ \mathrm{Fe^{2+}(aq) + 2\,OH^-(aq) \longrightarrow Fe(OH)_2(s, green)\downarrow}.\end{gathered}$$

Figure 5.1.1: Precipitation of iron ions and chromium ions, as $Fe(OH)_3$, $Fe(OH)_2$, and $Cr(OH)_3$ in the presence by OH^- at pH ~9.

The concentration of Fe^{2+}, i.e., the most soluble hydroxide of group III cations, is reduced by more than 99.99%, i.e., from 0.1M to 4.9 x 10^{-7} M when pH is increased to 9 and OH^- concentration is increased to 1 x 10^{-5} M:

$$\mathrm{Fe^{2+}} = \frac{\mathrm{K_{sp}}}{[\mathrm{OH^-}]^2} = \frac{4.9\times10^{-17}}{(1\times10^{-5})^2} = 4.9\times10^{-7}\ \mathrm{M}$$

Caution

Nickle ion is not precipitated at this stage as it forms soluble coordination cation $[Ni(NH_3)_6]^{2+}$ with ammonia:

$$\mathrm{Ni^{2+}(aq, green) + 6\,NH_3(aq) \rightleftharpoons Ni(NH_3)_6(aq, blue)}$$

Therefore, S^{2-} is introduced by adding thioacetamide and heating the mixture in a boiling water bath. Decomposition of thioacetamide produces ~0.01M H_2S:

$$\mathrm{CH_3CSNH_2(aq) + 2\,H_2O(l) \rightleftharpoons CH_3COO^-(aq) + NH_4^+(aq) + H_2S(aq)}$$

Nearly all of the H_2S dissociates to form ~0.01M S^{2-} at pH ~9:

$$\mathrm{H_2S(aq) + 2\,H_2O(l) \rightleftharpoons 2\,H_3O^+(aq) + S^{2-}(aq)} \quad K_a = \frac{[\mathrm{H_3O^+}]^2[\mathrm{S^{2-}}]}{[\mathrm{H_2\,S}]} = 1.3\times10^{-20}$$

The ammonia complex of nickel, i.e., $[Ni(NH_3)_6]^{2+}$ precipitates out as NiS, and, at the same time, $Fe(OH)_3$ and $Fe(OH)_2$ also convert to Fe_2S_3 and FeS:

$$\begin{gathered}\mathrm{Ni(NH_3)_6^{2+}(aq, blue) + S^{2-}(aq) \rightleftharpoons NiS(s, black) + 6\,NH_3(aq)}\\ \mathrm{2\,Fe(OH)_3(s, reddish{-}brown) + 3\,S^{2-}(aq) \rightleftharpoons Fe_2S_3(s, yellow{-}green) + 6\,OH^-(aq)}\end{gathered}$$

$$\mathrm{Fe(OH)_2(s, geen) + S^{2-}(aq) \rightleftharpoons FeS(s, black) + 2\,OH^-(aq)}$$

Chromium remains as $\mathrm{Cr(OH)_3}$ precipitate because chromium sulfide is unstable in water.

Group III precipitates, i.e., $\mathrm{Cr(OH)_3(s, gray-green)}$, $\mathrm{NiS(s, black)}$, $\mathrm{Fe_2S_3(s, yellow-green)}$, and $\mathrm{FeS(s, black)}$ in the mixture are separated as precipitates, and the rest of the ions, i.e, $\mathrm{Ca^{2+}}$, $\mathrm{Ba^{2+}}$, $\mathrm{Na^+}$ and $\mathrm{K^+}$, etc. remain dissolved in the supernatant, as shown in Figure 5.1.2. The color of the precipitate does not give a clear indication of what ions are present at this stage as several species of different colors may be mixed at this stage.

Figure 5.1.2: Group III precipitates, i.e., $\mathrm{Cr(OH)_3(s, gray-green)}$, $\mathrm{NiS(s, black)}$, $\mathrm{Fe_2S_3(s, yellow-green)}$, and $\mathrm{FeS(s, black)}$ in the mixture before centrifuge (left) and separated as a pellet at the bottom of the test tube after centrifuge (right).

5.2: Separation and confirmation if individual ions in group III precipitates

Separating and confirming nickel(II) ion

Acid like HCl dissolves precipitates of group III cations, i.e., $\mathrm{Cr(OH)_3(s, gray-green)}$, $\mathrm{Fe_2S_3(s, yellow-green)}$, and $\mathrm{FeS(s, black)}$, by the following series of reactions:

$$\mathrm{Cr(OH)_3(s, gray-green) \rightleftharpoons Cr^{3+}(aq) + 3\,OH^-(aq)}$$

$$\mathrm{FeS(s, black) \rightleftharpoons Fe^{2+}(aq) + 2\,S^{2-}(aq)}$$

$$\mathrm{Fe_2S_3(s, yellow-green) \rightleftharpoons 2\,Fe^{3+}(aq) + 3\,S^{2-}(aq)}$$

$$\mathrm{2\,Fe^{3+}(aq) + 2\,S^{2-}(aq) + 2\,H_3O^+ \rightleftharpoons 2\,Fe^{2+}(aq) + H_2S(aq) + S(s) + 2\,H_2O(l)}$$

$$\mathrm{3\,OH^-(aq) + 3\,H_3O^+ \rightleftharpoons +6\,H_2O(l)}$$

$$\mathrm{3\,S^{2-}(aq) + 6\,H_3O^+ \rightleftharpoons 3\,H_2S(aq) + 6\,H_2O(l)}$$

> $$\text{Overall reaction: } \mathrm{Cr(OH)_3(s, gray-green) + FeS(s, black) + Fe_2S_3(s, yellow-green) + 11\,H_3O^+ \rightleftharpoons Cr^{3+}(aq) + 3\,Fe^{2+}(aq) + 4\,H_2S(aq) + S(s) + 14\,H_2O(l)}$$

Removal of basic $\mathrm{OH^-}$ and $\mathrm{S^{2-}}$ ions from products by acid-base neutralization drives these reactions in the forward direction. $\mathrm{Fe^{3+}}$ is reduced to $\mathrm{Fe^{2+}}$ by $\mathrm{S^{2-}}$ under the acidic condition.

> The solubility of NiS is very low and it does not dissolve in non-oxidizing acid like HCl.

Therefore, the supernatant separated at this stage contains $\mathrm{Cr^{3+}}$ and $\mathrm{Fe^{2+}}$ and precipitate, if present is NiS, as shown in Figure 5.2.1.

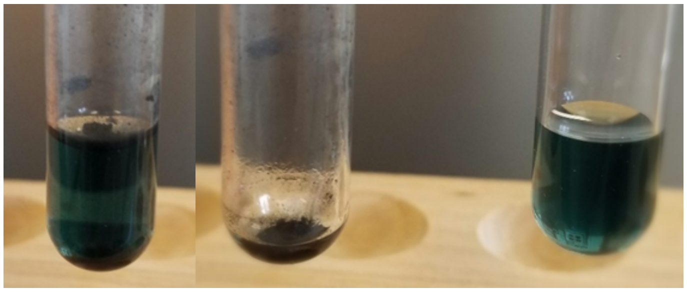


Figure 5.2.1: Group III mixture after heating with HCl solution (right), NiS precipitate (middle), and the supernatant containing $\mathrm{Cr^{3+}}$ and $\mathrm{Fe^{2+}}$ (right) separated by aspiration with the cotton-plug technique after centrifugation.

> **Aqua regia**, i.e., a mixture of HCl and $\mathrm{HNO_3}$, can dissolve NiS precipitate by removing $\mathrm{Ni^{2+}}$ as soluble coordination anion $\mathrm{[NiCl_4]^{2-}}$ and, at the the same time, removing $\mathrm{S^{2-}}$ by oxidizing it, using $\mathrm{NO_3^-}$ as oxidizing agent in the acidic medium.

$$\mathrm{NiS(s, black) \rightleftharpoons Ni^{2+}(aq) + 2\,S^{2-}(aq)}$$

$$\mathrm{Ni^{2+}(aq) + 4\,Cl^-(aq) \rightleftharpoons [NiCl_4]^{2-}(aq)}$$

$$\mathrm{3\,S^{2-}(aq) + 2\,NO_3^-(aq) + 8\,H_3O^+(aq) \rightleftharpoons 3\,S(s)\downarrow + 2\,NO(g)\uparrow + 12\,H_2O(l)}$$

Nitrogen oxide (NO) evaporates from the liquid mixture further driving the equilibrium to the forward direction. Most of the NO in air is oxidized to nitrogen dioxide ($\mathrm{NO_2}$) that forms brown color fumes over the liquid mixture as shown in Figure 5.2.2:

$$\mathrm{2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g, red-brown)}$$

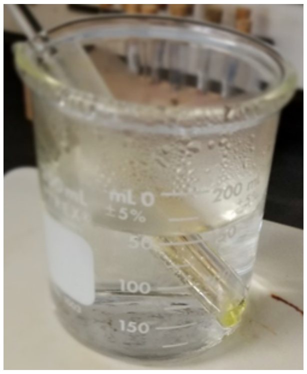


Figure 5.2.2: NiS being dissolved in aqua-regia as $[\mathrm{NiCl_4}]^{2-}$ coordination anion, $\mathrm{S^{2-}}$ oxidized to yellowish S particles, $\mathrm{NO_3^-}$ reduced to NO and then oxidized to brown color gas $\mathrm{NO_2}$ in the air above the mixture.

The S precipitates are removed by centrifugation and decantation. The $[\mathrm{NiCl_4}]^{2-}$ coordination anion is converted to $[\mathrm{Ni(NH_3)}]^{2+}$ coordination cation by making the solution alkaline by ammonia addition:

$$[\mathrm{NiCl_4}]^{2-}(\mathrm{aq}) + 6\,\mathrm{NH_3}(\mathrm{aq}) \rightleftharpoons [\mathrm{Ni(NH_3)_6}]^{2+}(\mathrm{aq, blue}) + 4\,\mathrm{Cl^-}(\mathrm{aq})$$

Dimethyl glyoxime $\mathrm{(CH_3)_2C_2(NOH)_2}$ is a ligand that is capable of forming two coordinate covalent bonds with transition metal ions. The ligands like $\mathrm{Cl^-}$, $\mathrm{NH_3}$, $\mathrm{H_2O}$, etc. that form one coordinate covalent bond with transition metals are called mono-dentate, and the chelates like dimethyl glyoxime form two coordinate covalent bonds are called bidentate. The ligands that can form two or more coordinate covalent bonds are called chelates or chelating agents. Coordination complexes with chelates are usually more stable, i.e., have higher formation constants than with mono-dentate ligands.

> The addition of dimethyl glyoxime $\mathrm{(CH_3)_2C_2(NOH)_2}$ to the liquid mixture containing $[\mathrm{Ni(NH_3)_6}]^{2+}$ in an alkaline medium forms an insoluble coordination compound $\mathrm{NiC_8H_{14}O_4}$ that separates as a red color precipitate, as shown in Figure 5.2.3:

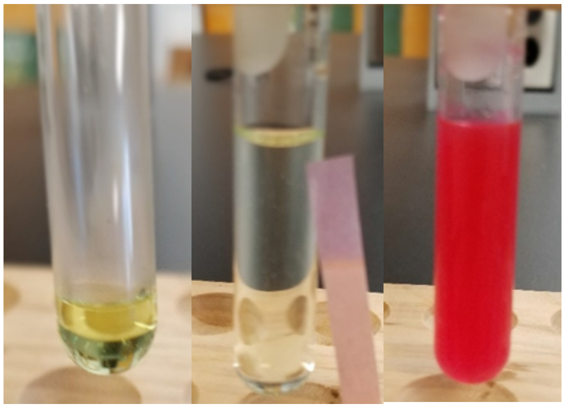


Figure 5.2.3: Clear solution containing $[\mathrm{Ni(NH_3)_6}]^{2+}$ ions obtained after dissolving NiS in aqua-regia (left), the $[[\mathrm{NiCl_4}]^{2-}$ converted to $[\mathrm{Ni(NH_3)_6}]^{2+}$ by making the solution alkaline by ammonia addition (middle), and red precipitate $\mathrm{NiC_8H_{14}O_4}$ formed by adding dimethylglyoxime to the solution.

The structure of the dimethyl glyoxime chelating agent and its coordination complex with nickel is illustrated in Figure 5.2.4 below.

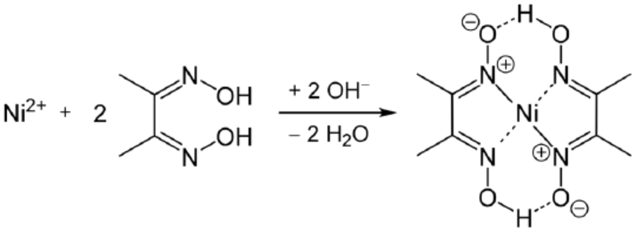


Figure 5.2.4: Reaction of Ni^{2+} with dimethyl glyoxime forming a red color coordination compound in confirmation test of nickel ion. Four coordinate covalent bonds formed in the complex between nickel and nitrogen atoms by the donation of lone pair of electrons on nitrogen are shown in the product.

The formation of red color precipitate upon the addition of dimethyl glyoxime at this stage confirms the presence of nickel ion in the test sample.

Separating and confirming iron ions

The supernatant containing Fe^{2+} and Cr^{3+} ions is separated from NiS precipitate after the addition of HCl to the precipitates of group III cations. The supernatant is made alkaline to pH 9 to 10 by adding ammonia solution. A pH paper is used to determine the pH. Hydrogen peroxide (H_2O_2) is added as an oxidizing agent to the alkaline solution. Fe^{2+} is oxidized to Fe^{3+} and precipitates out as rusty-brown solid $Fe(OH)_3$, and Cr^{3+} is oxidized to soluble chromate ion (CrO_4^{2-}) under this condition:

$$2\,Fe^{2+}(aq) + H_2O_2(aq) \rightleftharpoons 2\,Fe^{3+}(aq) + 2\,OH^-(aq)$$

$$Fe^{3+}(aq) + 3\,OH^-(aq) \rightleftharpoons Fe(OH)_3(s, rusty-brown)\downarrow$$

$$2\,Cr^{3+}(aq) + 3\,H_2O_2(aq) + 10\,OH^-(aq) \rightleftharpoons 2\,CrO_4^{2-}(aq) + 8\,H_2O(l)$$

The mixture is centrifuged to separate supernatant containing CrO_4^{2-} ions and precipitate containing rusty brown precipitate $Fe(OH)_3$, as shown in Figure 5.2.5.

Figure 5.2.5: Solution containing Fe^{2+} and Cr^{3+} is made alkaline to pH 9 to 10 by adding ammonia (left), Fe^{2+} is oxidized and precipitated out as rusty-brown $Fe(OH)_3$ (middle) and separated from a clear yellow solution containing CrO_4^{2-} (right) obtained by oxidation of Cr^{3+} with hydrogen peroxide. Hydrogen peroxide is being destroyed by heating to oxygen gas that can be seen bubbling out of the mixture in the middle image.

The $Fe(OH)_3$ precipitate is dissolved in HCl solution:

$$Fe(OH)_3(s, rusty-brown) \rightleftharpoons Fe^{3+}(aq) + 3\,OH^-(aq)$$

$$3\,OH^-(aq) + 3\,H_3O^+(aq) \rightleftharpoons 6\,H_2O(l)$$

> Thiocyanate (SCN^-) is a ligand that forms deep-red coordination complex ion $[FeSCN]^{2+}$ by reacting with Fe^{3+}, as shown in Figure 5.2.6.
>
> $$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [FeSCN]^{2+}(aq, deep-red)$$

Turning the supernatant color to deep-red upon addition of thiocyanate confirms iron ions are present in the test sample.

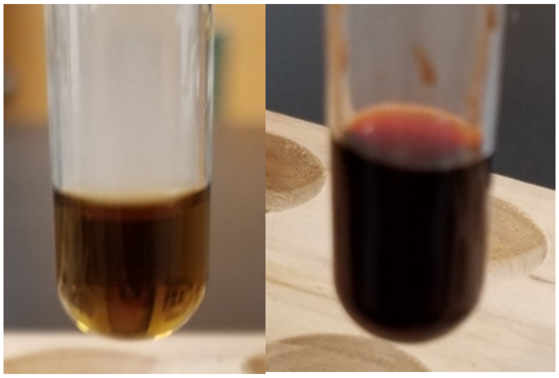


Figure 5.2.6: The $Fe(OH)_3$ precipitate dissolved in HCl (left) and forms deep-red color $[FeSCN]^{2+}$ by reacting with SCN^- (right).

Confirming chromium(III) ion

The supernatant obtained after removal of $Fe(OH)_3$ precipitate contains CrO_4^{2-} ions in an alkaline medium. The solution is made acidic by the addition of nitric acid where CrO_4^{2-} converts to dichromate ion ($Cr_2O_7^{2-}$):

$$2\,CrO_4^{2-}(aq) + 2\,H_3O^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + 3\,H_2O(l)$$

H_2O_2 is a reducing agent in acidic medium. H_2O_2 is added to the acidic mixture to reduce $Cr_2O_7^{2-}$ to Cr^{3+} through the following reactions:

$$2\,Cr_2O_7^{2-}(aq) + 8\,H_2O_2(aq) + 4\,H_3O^+(aq) \rightleftharpoons 4\,CrO_5(aq, dark-blue) + 14\,H_2O(l)$$

$$4\,CrO_5(aq) + 12\,H_3O^+(aq) \rightleftharpoons 4\,Cr^{3+}(aq, light-blue) + 7\,O_2(g)\uparrow + 18\,H_2O(l)$$

Oxygen evolves from the mixture and can be observed as gas bubbles in the solution. CrO_5 intermediate is a dark blue color in which one oxygen is in -2 oxidation state and the other four oxygen are in -1 oxidation state. CrO_5 is unstable in solution and decomposes to Cr^{3+} which is a light blue color. Residual H_2O_2 is destroyed by heating the mixture in a boiling water bath, which can be observed through oxygen gas bubbling out. Keep in mind that the destruction of H_2O_2 is significantly slower in an acidic medium than in an alkaline medium. It may take a longer time to destroy H_2O_2 in the acidic medium. Then the solution is changed from acidic to alkaline by adding 6M NaOH to the mixture. Cr^{3+} precipitates out as gray-green $Cr(OH)_3$ solid:

$$Cr^{3+}(aq) + 3\,OH^-(aq) \rightleftharpoons Cr(OH)_3(s, gray-green)\downarrow$$

The formation of gray-green precipitate at this stage confirms Cr^{3+} is present in the test sample, as shown in Figure 5.2.7.

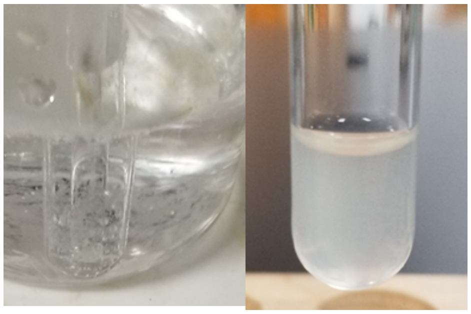


Figure 5.2.7: After oxidizing CrO_4^{2-} to Cr^{3+}, hydrogen peroxide is destroyed by heating which can be observed as oxygen gas bubbles leaving the mixture (left), and Cr^{3+} is confirmed by forming gray-green $Cr(OH)_3$ precipitate (right). Note: $Cr(OH)_3$ is usually formed in a very small amount at this stage making it difficult to detect.

5.3: Procedure, flowchart, and datasheets for separation and confirmation of group III cations

Table 1. List of chemicals and their hazards*

Chemical	Hazard
0.1M ammonium chloride (NH_4Cl)	Toxic and irritant
0.1M Chromium(III) chloride	Toxic and irritant
0.1M Iron(III) chloride	Toxic and corrosive
0.1M Nickel(II) chloride	Toxic, irritant, and suspected carcinogen

- *Hazards of 6M ammonia, 6M hydrochloric acid, 6M nitric acid, 3% hydrogen peroxide, and 1M thioacetamide are listed in chapter 2 in the commonly used reagent section. **Caution!** Used heavy metal ion solutions are disposed of in a labeled metal waste disposal container, do not drain these solutions down the drain.

Caution

- Used heavy metal ion solutions or precipitates are disposed of in a labeled metal waste disposal container, do not drain these solutions down the drain or in the regular trash.

Procedure for the analyses of group III cations

1. Take 15 drops of the fresh test solution if group I and group II cations are not present in the sample or **take the supernatant of step 1 of group II cations analysis**. Add 2 drops of 6M HCl. Then add 6M NH_3 drop by drop while stirring till the solution turns basic. Use red litmus paper to test -when it turns blue the solution is basic. Add 5 more drops of 6M NH_3 after the solution becomes alkaline to make NH_3/NH_4^+ buffer. Record the observations in the datasheet.
2. Add 10 drops of 1M thioacetamide to the solution from step 1, stir, and heat in a boiling water bath for 10 min. Then centrifuge for 2 min and decant. **Keep the supernatant for group IV** cations analysis and **keep the precipitate** for group III cations. Record the observations in the datasheet.
3. Wash the group III precipitates from step 2 by re-suspending in 15 drops of 0.1M NH_4Cl. Then centrifuge, decant, and discard the supernatant that is just the washing liquid. Re-suspend the precipitates in 10 drops of 6M HCl, heat for 2 min in a boiling water bath, centrifuge for two minutes, and **keep the supernatant** that may contain Fe^{2+} and/or Cr^{3+} and **keep the precipitate**, if there is any. Record the observations in the datasheet.
4. Wash the precipitate of step 3 by re-suspending it in 15 drops of distilled water. Then centrifuge for 1 min, decant and discard the supernatant that is just the washing liquid. Re-suspend the precipitate after adding 4 drops of 6M HCl and 6 drops of 6M HNO_3 (i.e., aqua regia). Heat the suspension in a boiling water bath for 2 min, then centrifuge for 2 min, decant, and discard the precipitate which is solid sulfur that contains no ions in it, but **keep the supernatant** for nickel analysis.
5. Use the cotton-plug technique to aspirate clear supernatant if it is not already a clear solution. Add 6M NH_3 to the clear supernatant drop by drop till the solution turns alkaline. Use red litmus paper to test -when it turns blue the solution is alkaline. If the solution turns turbid at this stage, centrifuge for 1 min, decant and discard the precipitate, but **keep the supernatant**.
6. Add 5 drops of dimethylglyoxime to the clear solution of step 5, stir, and leave for a minute. If a bright red precipitate is formed at this stage, it confirms Ni^{2+} is present in the test sample. Discard the mixture in the metal waste container and record the observations in the datasheet.
7. Inspect the supernatant of step 3, if it is not clear make it clear using the cotton plug technique. Add 6M NH_3 drop-by-drop to the clear supernatant while stirring till the mixture until it turns alkaline and has pH in the range of 9 to 10. Use a pH paper (not a litmus paper) to determine the pH. Add 5 drops of 3% H_2O_2 to the alkaline solution, stir, and leave for half-min. Heat the mixture in a boiling water bath to destroy excess H_2O_2 till the oxygen gas bubbles stop evolving from the solution. It may take about 3 min or more. Centrifuge for 1 min and test again for pH with a pH paper -if pH is less than 9,

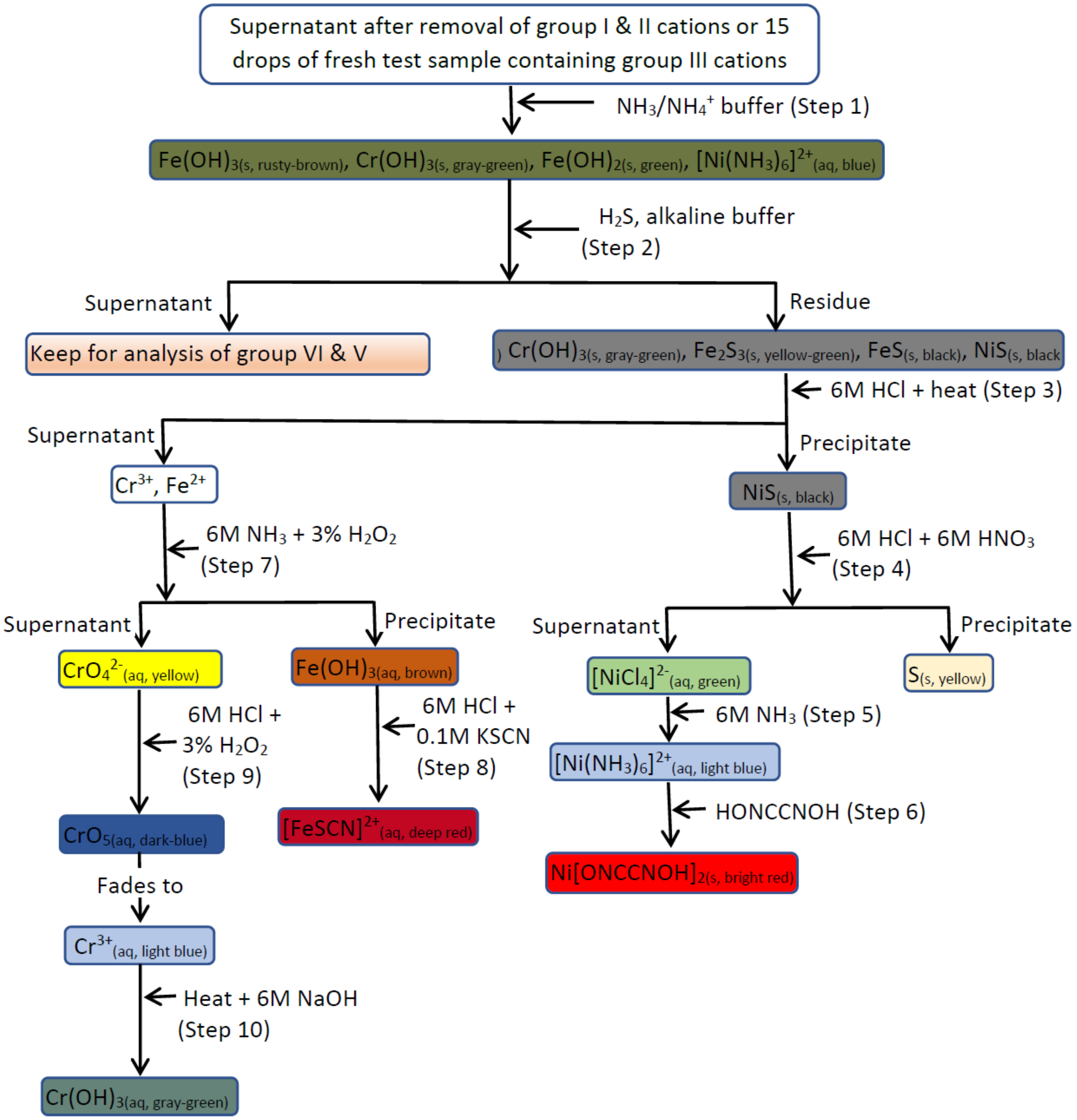
repeat this step 7 from the beginning, otherwise decant and **keep the supernatant** for analysis of chromium ions and **keep the precipitate**, there is any, for analysis of iron ions. Record the observations in the datasheet.

8. Dissolve the precipitate from step 7 in 5 drops of 6M HCl under stirring. Add 5 drops of distilled water to the solution followed by 5 drops of 0.1M potassium thiocyanate ($KSCN$) and stir to mix. If the solution color changes to deep red, it confirms iron ions are present in the test sample. Discard the mixture in a metal waste container, and record the observations in the datasheet.
9. To the supernatant of step 7 add 6M HNO_3 drop by drop till the solution becomes acidic with pH ~3. Use pH paper(not litmus paper) to determine the pH. Then add 1 drop of 3% H_2O_2, mix and leave for half-min. Then heat in boiling water bath to destroy excess H_2O_2 till oxygen bubbles stop forming in the mixture. It may take about 3 min or more. Cool the mixture by placing it in a room temperature water bath.
10. Add 6M $NaOH$ drop by drop to the solution of step 9 at room temperature till the solution is basic, i.e., turn red litmus paper to blue. The formation of gray-green precipitate at this stage confirms Cr^{3+} is present in the test sample. Caution: H_2O_2 decomposes slower in the acidic medium than in the basic medium. If the solution turns dark blue or yellow, it indicates chromium is present as CrO_5 or CrO_4^{2-} and H_2O_2 was not destroyed completely. In this case, add 6M HNO_3 drop by drop with stirring till the color fades away. Then repeat the addition of 6M NaOH till the solution turns basic and observe. The formation of gray-green precipitate at this stage confirms Cr^{3+} is present in the test sample. Discard the mixture in a metal waster container and record the observations in the datasheet.

Datasheets filling instructions for group III cations

1. Step number refers to the corresponding step number in the procedure sub-section.
2. In “the expected chemical reaction and expected observations column”, write an overall net ionic equation of the reaction that will happen if the ion being processed in the step was present, write the expected color change of the solution, the expected precipitate formed and its expected color, etc.
3. In the “the actual observations and conclusion” column write the color change, the precipitate formed and its color, etc. that is actually observed as evidence, and state the specific ion as present or absent.
4. In “the overall conclusion” row write one by one symbol of the ions being tested with a statement “present” or “absent” followed by evidence/s to support your conclusion.

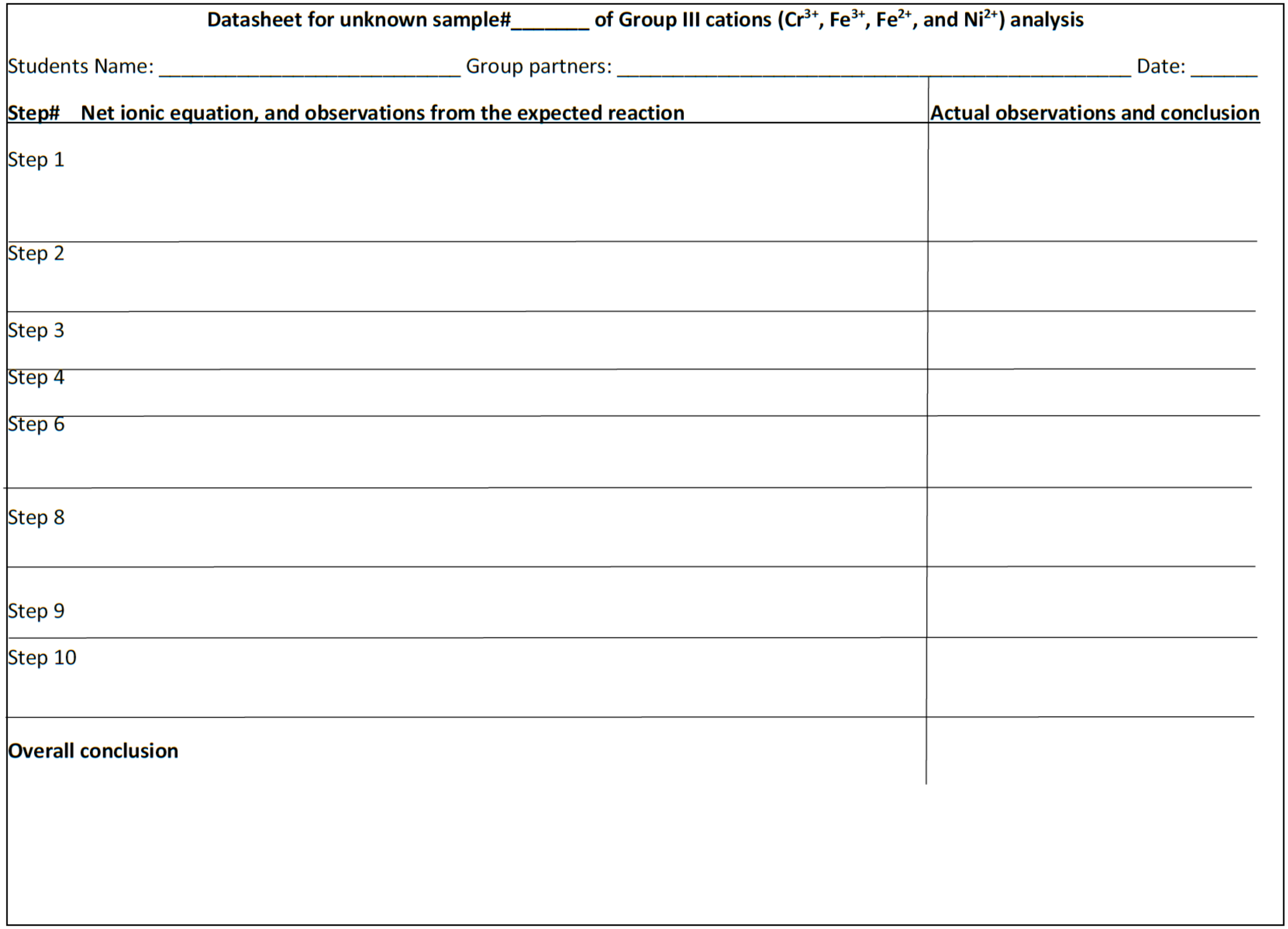
Group-III Cations Analysis Flow Chart



Data sheet for known Group III cations (Cr^{3+}, Fe^{3+}, Fe^{2+}, and Ni^{2+}) analysis

Students Name: ____________________________ Group partners: ____ Date: ______

Step# Net ionic equation, and observations from the expected reaction	**Actual observations and conclusion**
Step 1	
Step 2	
Step 3	
Step 4	
Step 6	
Step 8	
Step 9	
Step 10	
Overall conclusion	



Datasheet for unknown sample#_______ of Group III cations (Cr^{3+}, Fe^{3+}, Fe^{2+}, and Ni^{2+}) analysis

Students Name: ____________________________ Group partners: ____ Date: ______

Step#	**Net ionic equation, and observations from the expected reaction**	**Actual observations and conclusion**
Step 1		
Step 2		
Step 3		
Step 4		
Step 6		
Step 8		
Step 9		
Step 10		
Overall conclusion		

CHAPTER OVERVIEW

6: Group IV and Group V cations

6.1: Separating group IV cations

After removing chloride insoluble salts as the group I, and sulfide insoluble salts as group II and group III, the cations that may still be present in the solution from the initial mixture include Ca^{2+}, Ba^{2+}, Na^{+}, and K^{+}. Group IV comprises Ca^{2+} and Ba^{2+} that are separated from the other two ions based on the insoluble ions rule#2 described in chapter 1 which states “Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), and oxide (O^{2-}) are insoluble with the exception of alkali metals and ammonia.” Carbonate ion is introduced as ammonium carbonate ($(NH_4)_2CO_3$):

$$(NH_4)_2CO_3(s) + 2\,H_2O(l) \longrightarrow 2\,NH_4^{+}(aq) + CO_3^{2-}(aq)$$

> Addition of $(NH_4)_2CO_3$ solution cause precipitation of Ca^{2+} and Ba^{2+} as white precipitates $CaCO_3$ and $BaCO_3$, as shown in Figure $6.1.1$:
>
> $$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons CaCO_3(s, white)\downarrow \quad K_{sp} = 6\times10^{-9}$$
>
> $$Ba^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons BaCO_3(s, white)\downarrow \quad K_{sp} = 3\times10^{-9}$$

The precipitates of group IV cations are separated by centrifugation and decantation. The precipitate is used to separate and confirm group IV cations and the supernatant is kept for the analysis of group V cations.

Figure $6.1.1$: Group IV precipitates, $CaCO_3$ and $BaCO_3$.

6.2: Separation and confirmation of individual ions in group IV precipitates and group V mixture

Separating and confirming barium ion

The precipitates of Group IV cations, i.e., $CaCO_3$ and $BaCO_3$ are soluble in acidic medium. In these experiments acetic acid CH_3COOH is used to make the solution acidic that results in the dissolution of $CaCO_3$ and $BaCO_3$:

$$4\,CH_3COOH(aq) + 4\,H_2O(l) \rightleftharpoons 4\,CH_3COO^-(aq) + 4\,H_3O^+(aq)$$

$$CaCO_3(s, white) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

$$BaCO_3(s, white) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$$

$$2\,CO_3^{2-}(aq) + 4\,H_3O^+(aq) \rightleftharpoons 2\,H_2CO_3(aq) + 4\,H_2O(l)$$

$$2\,H_2CO_3(aq) \rightleftharpoons 2\,H_2O(l) + 2\,CO_2(g)\uparrow$$

$$\text{Overall reaction: } 4\,CH_3COOH(aq) + CaCO_3(s, white) + BaCO_3(s, white) \rightleftharpoons 4\,CH_3COO^-(aq) + Ca^{2+} + Ba^{2+} + 2\,H_2O(l) + 4\,CO_2(g)\uparrow$$

CO_3^{2-} ion is a weak base that reacts with H_3O^+ and forms carbonic acid (H_2CO_3. Carbonic acid is unstable in water and decomposes into carbon dioxide and water. Carbon dioxide leaves the solution that drives the reactions forward, as shown in Figure 6.2.1.

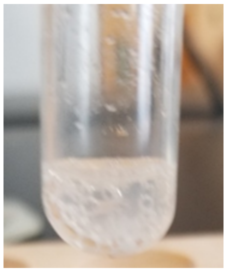


Figure 6.2.1: Group V precipitate dissolved with the evolution of carbon dioxide upon addition of acetic acid.

> The Acetate ion (CH_3COO^-) produced in the above reactions is a conjugate base of a weak acid acetic acid (CH_3COOH). More acetic acid is added to the solution to make a CH_3COOH/CH_3COO^- buffer that can maintain pH at ~5.

Potassium chromate (K_2CrO_4) solution is added at this stage that introduces chromate ion CrO_4^{2-}:

$$K_2CrO_4(s) \rightleftharpoons 2\,K^+(aq) + CrO_4^{2-}(aq)$$

Although both calcium and barium ions form insoluble salt with chromate ion ($CaCrO_4$ K_{sp} = 7.1 x 10^{-4} and $BaCrO_4$ K_{sp} = 1.8 x 10^{-10}), $BaCrO_4$ is less soluble and can be selectively precipitated by controlling CrO_4^{2-} concentration. The chromate ion is involved in the following pH dependent equilibrium:

$$2\,CrO_4^{2-}(aq) + 2\,H_3O^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + 3\,H_2O(l) \quad K = 4.0 \times 10^{14}$$

At pH ~5 in a CH_3COOH/CH_3COO^- buffer, the concentration of CrO_4^{2-} is enough to selectively precipitate barium ions leaving calcium ions in the solution:

$$Ba^{2+}(aq) + CrO_4^{2-}(aq) \rightleftharpoons BaCrO_4(s, light\ yellow)\downarrow$$

The mixture is centrifuged and decanted to separate $BaCrO_4$ precipitate from the supernatant containing Ca^{2+} ions as shown in Figure 6.2.2. Although the formation of a light yellow precipitate ($BaCrO_4$) at this stage is a strong indication that Ba^{2+} is present in the test sample, Ca^{2+} may also form a light yellow precipitate ($CaCrO_4$), particularly if pH is higher than the recommended value of 5.

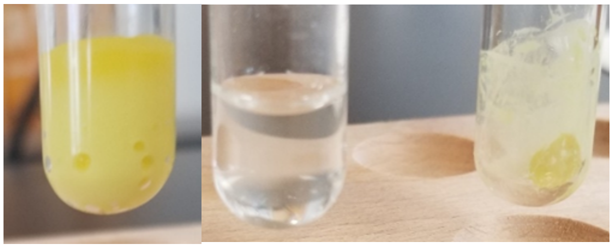


Figure 6.2.2: Selective precipitation of $BaCrO_4$ by adding CrO_4^{2-} at pH ~5 leaving Ca^{2+} in the solution(left) and supernatant (middle) separated from precipitate (right) after centrifugation and decantation.

Group IV and V cations are most often confirmed by the flame test. Figure 6.2.3 shows the flame test results of group IV cations. The presence of barium is further confirmed by a flame test. For this purpose, $BaCrO_4$ precipitate is treated with 12M HCl. The concentrated HCl removes CrO_4^{2-} by converting it to dichromate ($Cr_2O_7^{2-}$) that resulting in the dissolution of $BaCrO_4$:

$$2\,BaCrO_4(s,\text{light yellow}) \rightleftharpoons 2\,Ba^{2+}(aq) + 2\,CrO_4^{2-}(aq)$$

$$2\,CrO_4^{2-}(aq) + 2\,H_3O^{+}(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + 3\,H_2O(l)$$

A flame test is applied to the solution. Ba^{2+} imparts characteristic yellow-green color to the flame. If the yellow-green color is observed in the flame test, it confirms Ba^{2+} is present in the test sample.

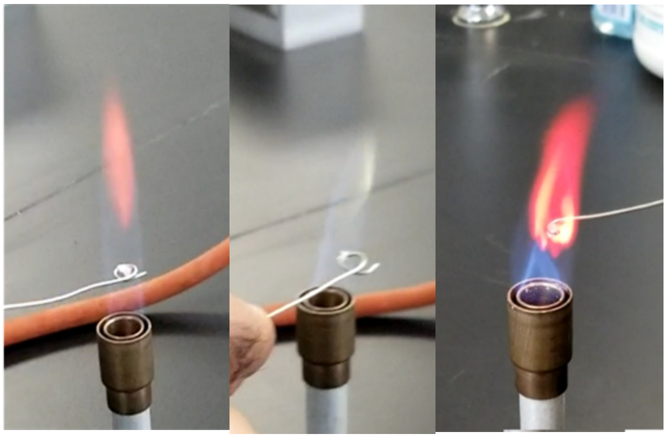


Figure 6.2.3: Flame test of group IV cations, i.e., calcium (left), barium (middle), and strontium (right).

Confirming calcium ion

> The Ca^{2+} present in the supernatant is precipitated by adding oxalate ion ($C_2O_4^{2-}$):
>
> $$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \rightleftharpoons CaC_2O_4(s,\text{white})\downarrow$$

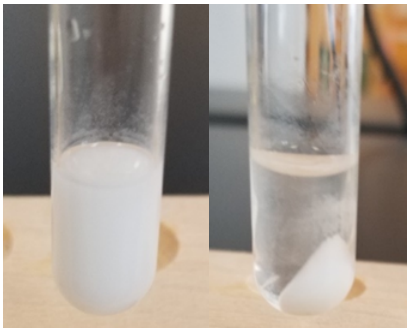


Figure 6.2.4: Calcium oxalate precipitate before (left) and after (right) centrifugation.

The formation of white precipitate, i.e., CaC_2O_4 shown in Figure 6.2.4, is a strong indication that Ca^{2+} is present in the test sample. However, if Ba^{2+} is not fully separated earlier, it also forms a white precipitate BaC_2O_4. The presence of Ca^{2+} is further verified by flame test. For this purpose, the precipitate is dissolved in 6M HCl:

$$CaC_2O_4(s, white) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

$$C_2O_4^{2-}(aq) + 2\,H_3O^+(aq) \rightleftharpoons H_2C_2O_4(aq)$$

Strong acid like HCl increases H_3O^+ ion concentration that drives the above reaction forward based on Le Chatelier's principle. The flame test is applied to the solution. If Ca^{2+} is present in the solution, it imparts characteristic brick-red color to the flame, as shown in Fig. 6.2.3. Observation of the brick-red color in the flame test confirms the presence of Ca^{2+} in the test sample. The flame color changes to light green when seen through cobalt blue glass.

Confirming group V cations by the flame test

Group V cations, i.e., alkali metal, Na^+, K^+, etc. form soluble ionic compounds. Separation of alkali metals cations by selective precipitation is not possible using commonly available reagents. So, group V cations are not separated in these analyses. However, alkali metal cations impart characteristic color to the flame that helps in their confirmation as shown in Figure 6.2.5. The supernatant after separating group IV precipitate is concentrated by heating the solution to evaporate the solvent. A flame test is applied to the concentrated solution.

> Lithium imparts carmine red, sodium imparts intense yellow, and potassium imparts lilac color to the flame.

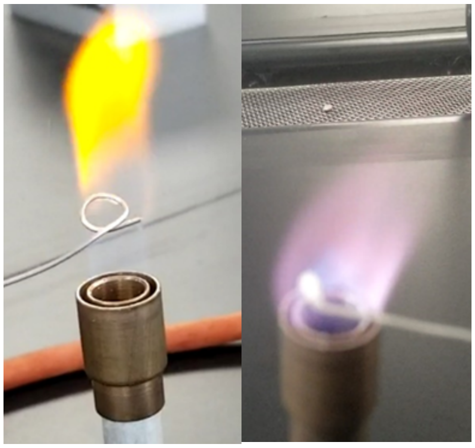


Figure 6.2.5: Flame tests of group V cations, sodium (left) and potassium (right).

6.3: Procedure, flowchart, and datasheets for separation and confirmation of group IV and group V cations

Table 1. List of chemicals and their hazards*

Chemical	Hazard
6M Acetic acid (CH_3COOH)	Toxic and corrosive
0.2M Ammonium oxalate	Irritant
0.1M Barium chloride	Highly toxic
0.1M Calcium chloride	Irritant
0.1M Potassium chromate	Suspected carcinogen

- *Hazards of 6M ammonia, 6M hydrochloric acid, 6M nitric acid, 3% hydrogen peroxide, and 1M thioacetamide are listed in chapter 2 in the commonly used reagent section. **Caution!** Used heavy metal ion solutions are disposed of in a Labeled metal waste disposal container, do not drain these solutions down the drain.

Caution

- Used heavy metal ion solutions or precipitates are disposed of in a labeled metal waste disposal container, do not drain these solutions down the drain or in the regular trash.

Procedure for the analyses of group IV and group V cations

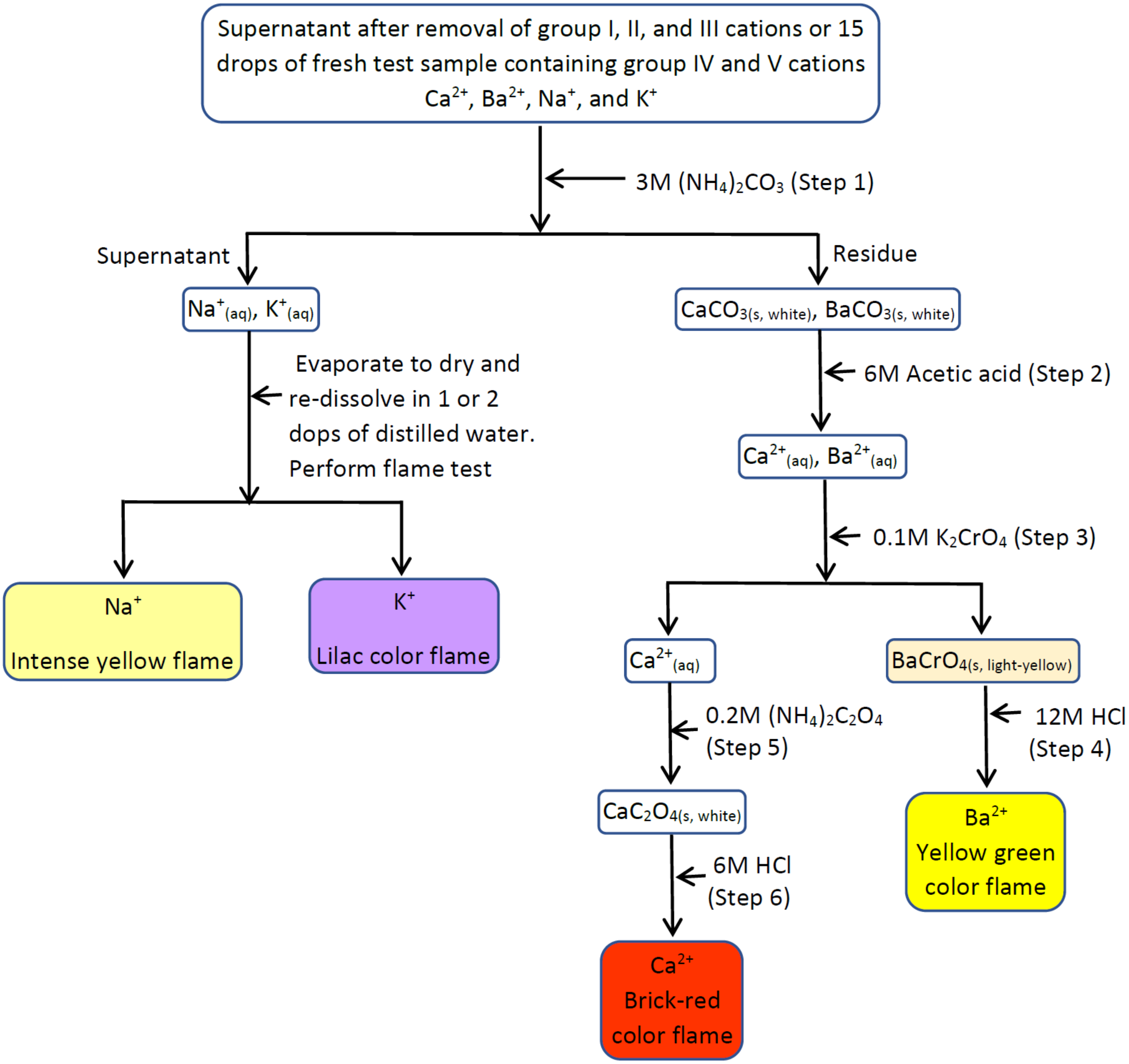
1. Take 15 drops of the fresh test solution if the group I to III cations are not present in the sample or **take the supernatant of step 2 of group III cations analysis**. Add 15 drops of 3M $(NH_4)_2CO_3$, stir to thoroughly mix using a clean glass rod, centrifuge for 2 min, decant and **keep the supernatant** for group V tests, and **keep the precipitate** for group IV cations analysis. Record the observations in the datasheet.
2. Wash the precipitate of step 1 by re-suspending it in 15 drops of distilled water under stirring, centrifuge for 2 min, decant and keep the precipitate and discard the supernatant which is just the washing liquid. Add 5 drops of 6M acetic acid to the precipitate and heat for half-min while stirring to dissolve the precipitate. Add 2 more drops of 6M acetic acid while heating and stirring if needed to fully dissolve the precipitate. After the precipitate has dissolved, add 3 more drops of 6M acetic acid to make a CH_3COOH/CH_3COO^- buffer. Record the observations in the datasheet.
3. Add 10 drops of 0.1M K_2CrO_4, stir to mix, and heat for 1 min. Immediately centrifuge for 2 min and decant while hot. **Keep the supernatant** for analysis of Ca^{2+}. If a light-yellow precipitate is formed at this stage it is most likely $BaCrO_4$ due to Ba^{2+} present in the test sample. **Keep the precipitate** for the flame test. Record the observations in the datasheet.
4. Wash the precipitate of step 2 by re-suspending it in 15 drops of distilled water, centrifuge for 2 min, decant, and discard the supernatant water which is just the washing solvent. Add 5 drops of 12M HCl to the precipitate, stir to mix, and heat in a boiling water bath for 2 min to dissolve the precipitate. Perform the flame test, i.e., dip a clean nichrome or platinum wire loop in the solution and then place the loop on the outer edge of a blue flame of a Bunsen burner, approximately halfway between the top and bottom of the flame and observe the flam color. If the solution imparts yellow-green color to the flame, it is due to barium ion confirming Ba^{2+} is present in the test sample. The nichrome wire can be re-used after dipping it in 6M HCl followed by making it red-hot in a flame. Repeat this process until the wire does not impart color to the flame. Then the wire can be re-used. Another approach is to cut off the end part of the wire that was dipped in the salt, make a new loop at the fresh end, and use it for the next flame test. Discard the solution in a metal waste container and record the observations in the datasheet.
5. To the supernatant from step 3, add 10 drops of 0.2M ammonium oxalate ($(NH_4)_2C_2O_4$), stir to mix, centrifuge for 2 min, decant, discard the supernatant and observe the precipitate. The formation of white precipitate at this stage is CaC_2O_4 which is a strong indication of Ca^{2+} is present in the test solution. **Keep the precipitate** for the flame test. Record the observation in the datasheet.

6. Dissolve the precipitate of step 5 in 3 drops of 6M HCl. Perform the flame test, i.e., dip a clean nichrome or platinum wire loop in the solution and then place the loop in the outer edge of a blue flame of a Bunsen burner, approximately halfway between the top and bottom of the flame and observe the flam color. If the solution imparts brick-red color to the flame, it is due to calcium ions confirming Ca^{2+} is present in the test sample. Discard the solution in the metal waste container and record the observations in the datasheet.
7. Group V cations: Evaporite excess water from the supernatant of step 1 by heating. If any solid residue is left it is due to group V cations, i.e., sodium, potassium, etc. Add a drop or two drops of water to dissolve the precipitate. Perform the flame test, i.e., dip a clean nichrome or platinum wire loop in the solution and then place the loop in the outer edge of a blue flame of a Bunsen burner, approximately halfway between the top and bottom of the flame and observe the flame color. If the solution imparts some color to the flame, it is due to group V cations: an intense yellow color flame confirms Na^{+} is present in the test solution, and purple or lilac color to the flame confirms K^{+} is present in the test solution. Discard the solution in the metal waster container and record your observations in the datasheet.

Datasheets filling instructions for group IV and group V cations

1. Step number refers to the corresponding step number in the procedure sub-section.
2. In “the expected chemical reaction and expected observations column”, write an overall net ionic equation of the reaction that will happen if the ion being processed in the step was present, write the expected color change of the solution, the expected precipitate formed and its expected color, etc.
3. In the “the actual observations and conclusion” column write the color change, the precipitate formed and its color, etc. that is actually observed as evidence, and state the specific ion as present or absent.
4. In “the overall conclusion” row write one by one symbol of the ions being tested with a statement “present” or “absent” followed by evidence/s to support your conclusion.

Group-IV and Group V Cations Analysis Flow



Data sheet for known Group IV cations (Ca^{2+} and Ba^{2+}) and Group V cations (Na^{+} and K^{+}) analysis

Students Name: ____________________________ Group partners: ____ Date: ______

Step#	Net ionic equation, and observations from the expected reaction	Actual observations and conclusion
Step 1		
Step 2		
Step 3		
Step 4		
Step 5		
Step 6		
Step 7		
Overall conclusion		

Data sheet for unknown sample#__________ of Group IV cations (Ca^{2+} and Ba^{2+}) and Group V cations (Na^{+} and K^{+}) analysis

Students Name: ______________________________ Group partners: ____ Date: _______

Step#	**Net ionic equation, and observations from the expected reaction**	**Actual observations and conclusion**
Step 1		
Step 2		
Step 3		
Step 4		
Step 5		
Step 6		
Step 7		
Overall conclusion		

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