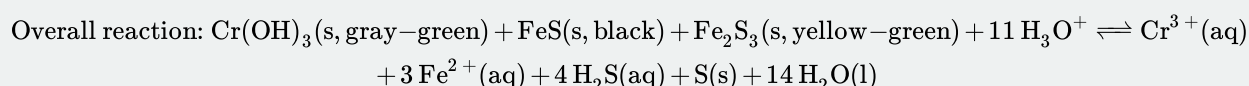
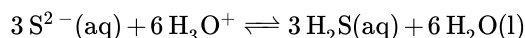
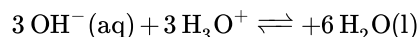
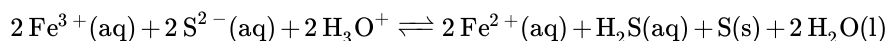
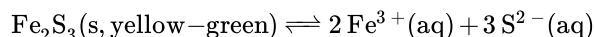
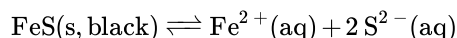
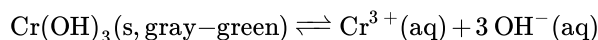


5.2: Separation and confirmation of individual ions in group III precipitates

Separating and confirming nickel(II) ion

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



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

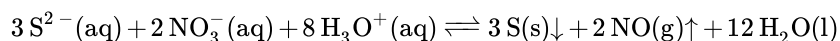
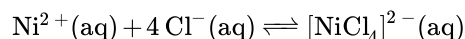
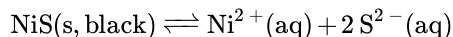
The solubility of NiS is very low and it does not dissolve in non-oxidizing acid like HCl.

Therefore, the supernatant separated at this stage contains Cr^{3+} and 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 Cr^{3+} and Fe^{2+} (left) separated by aspiration with the cotton-plug technique after centrifugation.

Aqua regia, i.e., a mixture of HCl and HNO_3 , can dissolve NiS precipitate by removing Ni^{2+} as soluble coordination anion $[\text{NiCl}_4]^{2-}$ and, at the same time, removing S^{2-} by oxidizing it, using NO_3^{-} as oxidizing agent in the acidic medium.



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 (NO_2) that forms brown color fumes over the liquid mixture as shown in Figure 5.2.2:

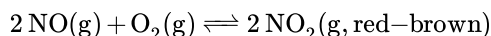
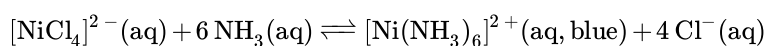




Figure 5.2.2: NiS being dissolved in aqua-regia as $[\text{NiCl}_4]^{2-}$ coordination anion, S^{2-} oxidized to yellowish S particles, NO_3^- reduced to NO and then oxidized to brown color gas NO_2 in the air above the mixture.

The S precipitates are removed by centrifugation and decantation. The $[\text{NiCl}_4]^{2-}$ coordination anion is converted to $[\text{Ni}(\text{NH}_3)_6]^{2+}$ coordination cation by making the solution alkaline by ammonia addition:



Dimethyl glyoxime $(\text{CH}_3)_2\text{C}_2(\text{NOH})_2$ is a ligand that is capable of forming two coordinate covalent bonds with transition metal ions. The ligands like Cl^- , NH_3 , 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 $(\text{CH}_3)_2\text{C}_2(\text{NOH})_2$ to the liquid mixture containing $[\text{Ni}(\text{NH}_3)_6]^{2+}$ in an alkaline medium forms an insoluble coordination compound $\text{NiC}_8\text{H}_{14}\text{O}_4$ that separates as a red color precipitate, as shown in Figure 5.2.3:



Figure 5.2.3: Clear solution containing $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ions obtained after dissolving NiS in aqua-regia (left), the $[\text{NiCl}_4]^{2-}$ converted to $[\text{Ni}(\text{NH}_3)_6]^{2+}$ by making the solution alkaline by ammonia addition (middle), and red precipitate $\text{NiC}_8\text{H}_{14}\text{O}_4$ 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.

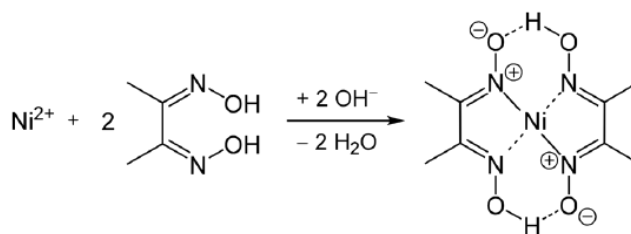
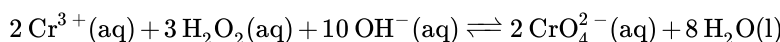
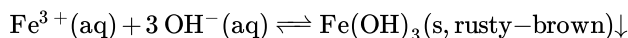
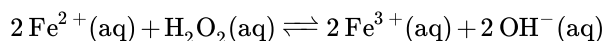


Figure 5.2.4: Reaction of Ni^{2+} with dimethyl glyoxime forming a red color coordination compound in confirmation test of nickel ion. Four coordinate covalent bonds formed in the complex between nickel and nitrogen atoms by the donation of lone pair of electrons on nitrogen are shown in the product.

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 $\text{Fe}(\text{OH})_3$, and Cr^{3+} is oxidized to soluble chromate ion (CrO_4^{2-}) under this condition:



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

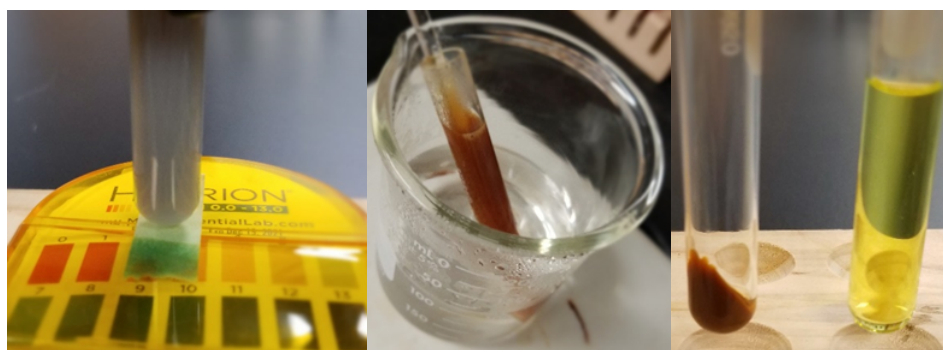
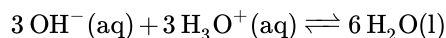
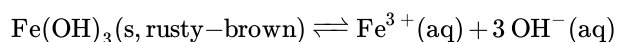
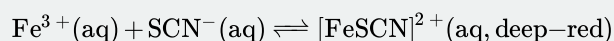


Figure 5.2.5: Solution containing Fe^{2+} and Cr^{3+} is made alkaline to pH 9 to 10 by adding ammonia (left), Fe^{2+} is oxidized and precipitated out as rusty-brown $\text{Fe}(\text{OH})_3$ (middle) and separated from a clear yellow solution containing CrO_4^{2-} (right) obtained by oxidation of Cr^{3+} 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 $\text{Fe}(\text{OH})_3$ precipitate is dissolved in HCl solution:



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



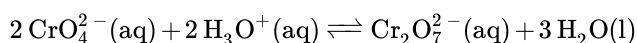
Turning the supernatant color to deep-red upon addition of thiocyanate confirms iron ions are present in the test sample.



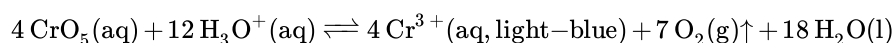
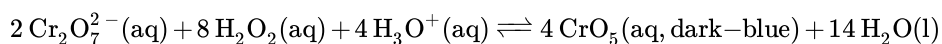
Figure 5.2.6: The $\text{Fe}(\text{OH})_3$ precipitate dissolved in HCl (left) and forms deep-red color $[\text{FeSCN}]^{2+}$ by reacting with SCN^- (right).

Confirming chromium(III) ion

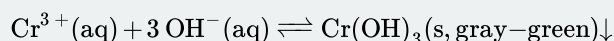
The supernatant obtained after removal of $\text{Fe}(\text{OH})_3$ precipitate contains CrO_4^{2-} ions in an alkaline medium. The solution is made acidic by the addition of nitric acid where CrO_4^{2-} converts to dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$):



H_2O_2 is a reducing agent in acidic medium. H_2O_2 is added to the acidic mixture to reduce $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+} through the following reactions:



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 $\text{Cr}(\text{OH})_3$ solid:



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.

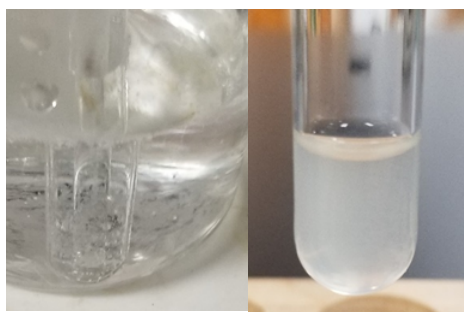


Figure 5.2.7: After oxidizing CrO_4^{2-} to Cr^{3+} , hydrogen peroxide is destroyed by heating which can be observed as oxygen gas bubbles leaving the mixture (left), and Cr^{3+} is confirmed by forming gray-green $\text{Cr}(\text{OH})_3$ precipitate (right). Note: $\text{Cr}(\text{OH})_3$ is usually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

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