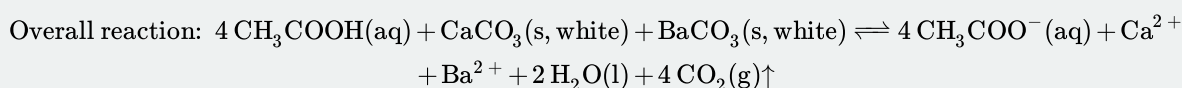
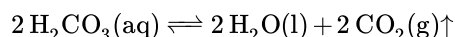
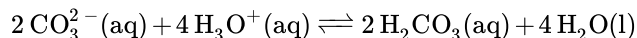
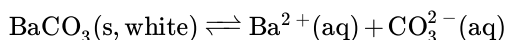
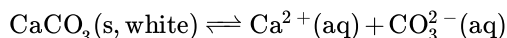
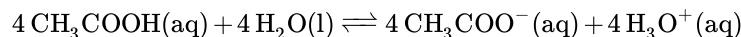


## 6.2: Separation and confirmation of individual ions in group IV precipitates and group V mixture

### Separating and confirming barium ion

The precipitates of Group IV cations, i.e.,  $\text{CaCO}_3$  and  $\text{BaCO}_3$  are soluble in acidic medium. In these experiments acetic acid  $\text{CH}_3\text{COOH}$  is used to make the solution acidic that results in the dissolution of  $\text{CaCO}_3$  and  $\text{BaCO}_3$ :



$\text{CO}_3^{2-}$  ion is a weak base that reacts with  $\text{H}_3\text{O}^+$  and forms carbonic acid ( $\text{H}_2\text{CO}_3$ ). 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.

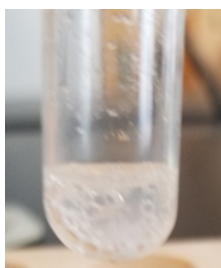
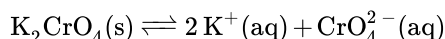


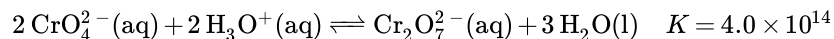
Figure 6.2.1: Group V precipitate dissolved with the evolution of carbon dioxide upon addition of acetic acid.

The Acetate ion ( $\text{CH}_3\text{COO}^-$ ) produced in the above reactions is a conjugate base of a weak acid acetic acid ( $\text{CH}_3\text{COOH}$ ). More acetic acid is added to the solution to make a  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$  buffer that can maintain  $pH$  at  $\sim 5$ .

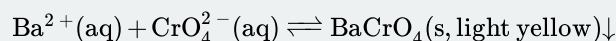
Potassium chromate ( $\text{K}_2\text{CrO}_4$ ) solution is added at this stage that introduces chromate ion  $\text{CrO}_4^{2-}$ :



Although both calcium and barium ions form insoluble salt with chromate ion ( $\text{CaCrO}_4$   $K_{sp} = 7.1 \times 10^{-4}$  and  $\text{BaCrO}_4$   $K_{sp} = 1.8 \times 10^{-10}$ ),  $\text{BaCrO}_4$  is less soluble and can be selectively precipitated by controlling  $\text{CrO}_4^{2-}$  concentration. The chromate ion is involved in the following  $pH$  dependent equilibrium:



At  $pH \sim 5$  in a  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$  buffer, the concentration of  $\text{CrO}_4^{2-}$  is enough to selectively precipitate barium ions leaving calcium ions in the solution:



The mixture is centrifuged and decanted to separate  $\text{BaCrO}_4$  precipitate from the supernatant containing  $\text{Ca}^{2+}$  ions as shown in Figure 6.2.2. Although the formation of a light yellow precipitate ( $\text{BaCrO}_4$ ) at this stage is a strong indication that  $\text{Ba}^{2+}$  is present in the test sample,  $\text{Ca}^{2+}$  may also form a light yellow precipitate ( $\text{CaCrO}_4$ ), particularly if pH is higher than the recommended value of 5.

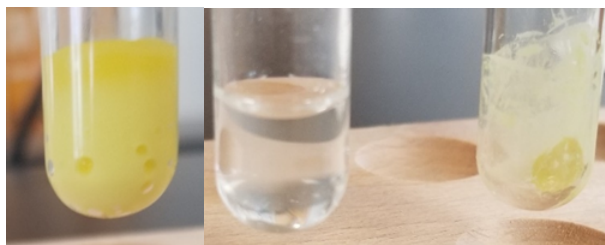
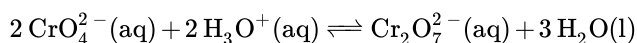
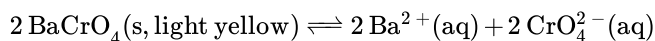


Figure 6.2.2: Selective precipitation of  $\text{BaCrO}_4$  by adding  $\text{CrO}_4^{2-}$  at pH ~5 leaving  $\text{Ca}^{2+}$  in the solution(left) and supernatant (middle) separated from precipitate (right) after centrifugation and decantation.

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,  $\text{BaCrO}_4$  precipitate is treated with 12M HCl. The concentrated HCl removes  $\text{CrO}_4^{2-}$  by converting it to dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) that resulting in the dissolution of  $\text{BaCrO}_4$ :



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

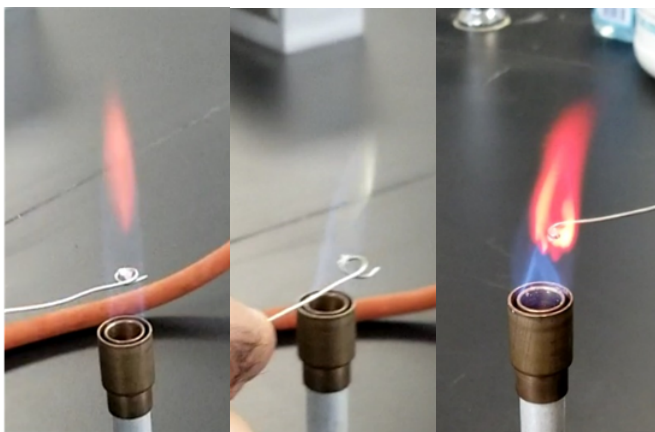
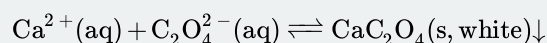


Figure 6.2.3: Flame test of group IV cations, i.e., calcium (left), barium (middle), and strontium (right).

### Confirming calcium ion

The  $\text{Ca}^{2+}$  present in the supernatant is precipitated by adding oxalate ion ( $\text{C}_2\text{O}_4^{2-}$ ):



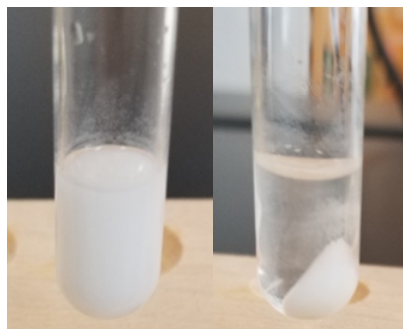
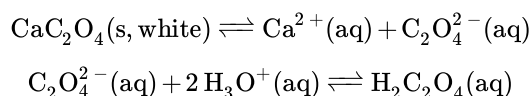


Figure 6.2.4: Calcium oxalate precipitate before (left) and after (right) centrifugation.

The formation of white precipitate, i.e.,  $\text{CaC}_2\text{O}_4$  shown in Figure 6.2.4, is a strong indication that  $\text{Ca}^{2+}$  is present in the test sample. However, if  $\text{Ba}^{2+}$  is not fully separated earlier, it also forms a white precipitate  $\text{BaC}_2\text{O}_4$ . The presence of  $\text{Ca}^{2+}$  is further verified by flame test. For this purpose, the precipitate is dissolved in 6M HCl:



Strong acid like HCl increases  $\text{H}_3\text{O}^+$  ion concentration that drives the above reaction forward based on Le Chatelier's principle. The flame test is applied to the solution. If  $\text{Ca}^{2+}$  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  $\text{Ca}^{2+}$  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,  $\text{Na}^+$ ,  $\text{K}^+$ , 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.

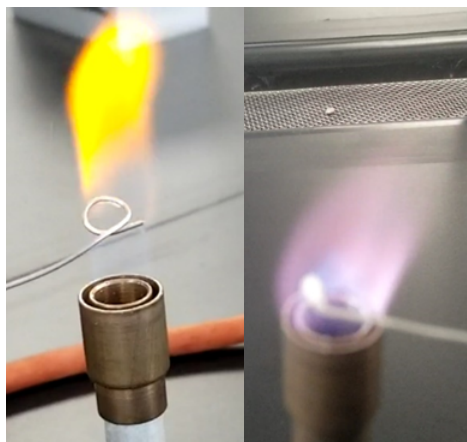


Figure 6.2.5: Flame tests of group V cations, sodium (left) and potassium (right).

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