

Group IV Cations

(Alkaline Earth Metals)

Barium (II), Strontium (II), Calcium (II)

This group of cations also called the alkaline earth group is composed of three elements: barium, strontium and calcium. These three elements occur within the same group of the periodic table and their cations are therefore closely related in their chemical reactions. This renders a clean separation from each other not feasible. However, for qualitative analysis, the carbonates, chromates, sulphates and oxalates are found useful. Thus, all three metal cations are precipitated as carbonates, then they are separated by precipitating barium as chromate, strontium as sulphate and calcium as oxalate with the help of certain

reagents or masking agents. Since the values of the solubility product constants of each of these cations with the three precipitating anions are too close to permit sharp separation and identification, it is necessary, for confirmation of these precipitates and their corresponding cations to employ the flame tests, as they are more specific especially by comparison with known solutions of these cations.

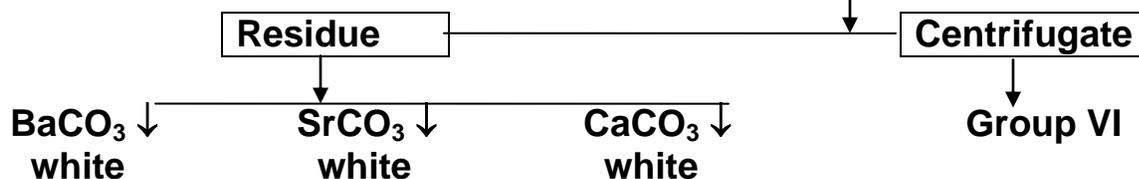
Group reagent

Ammonium carbonate solution in presence of ammonium hydroxide and ammonium chloride. The reagent has to be used in neutral or slightly alkaline media and is decomposed by acids (even by acetic acid) with the formation of carbon dioxide.

The white precipitates formed with the group reagent are : barium carbonate BaCO_3 , strontium carbonate SrCO_3 and calcium carbonate CaCO_3 .

Separation of Group IV cations
 Ba^{2+} , Sr^{2+} , Ca^{2+}

- Add solid NH_4Cl and dissolve
- Add Conc. NH_4OH + $(NH_4)_2CO_3$ solution (1)
- Heat at $60-70^\circ C$ in a w.b. (2)
- Centrifuge

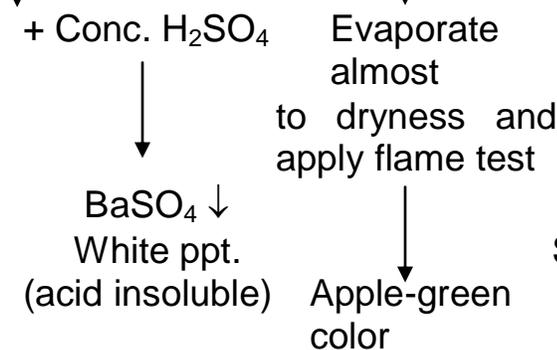


- Wash with hot water
- Dissolve in acetate buffer (acetic acid/ammonium acetate) (3)
- Heat to boiling
- Add a slight xss of K_2CrO_4 solution
- Centrifuge



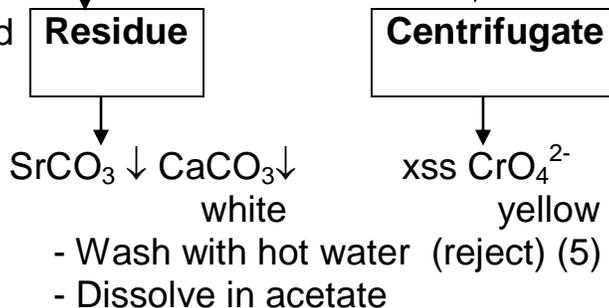
$BaCrO_4$ ↓
yellow

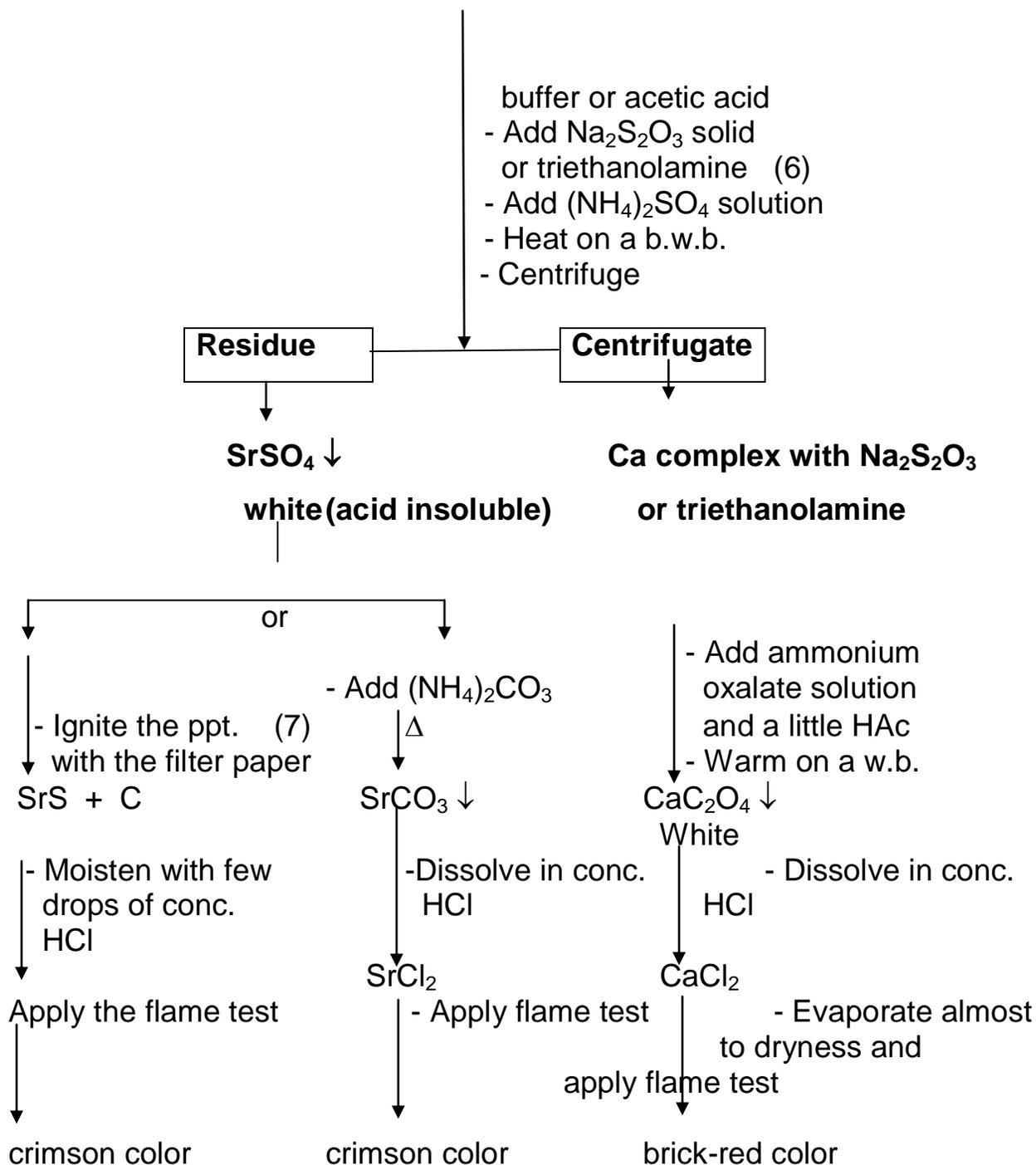
- Wash with hot water
- Dissolve in conc. HCl
- Divide into 2 portions



$Sr(Ac)_2$, $Ca(Ac)_2$, xss K_2CrO_4

- Alkalinize with conc. NH_4OH
- Add $(NH_4)_2CO_3$ solution or solid Na_2CO_3 (4)
- Heat, Centrifuge





Notes :

(1) Ammonium chloride is added to prevent the precipitation of $\text{Mg}(\text{OH})_2$ or $\text{Mg}(\text{CO}_3)$ by decreasing the concentration of (OH^-) from ammonia solution and (CO_3^{2-}) from ammonium carbonate solution through common ion effect. So, in ammonium carbonate solutions having the (CO_3^{2-}) regulated by the presence of both NH_4^+ ions and free NH_3 in moderately high concentrations, Mg^{2+} ion remains in solution.

If NH_4^+ ion is present and NH_3 is absent, the (CO_3^{2-}) will be decreased to such a low value that CaCO_3 will not be completely precipitated.

(2) Commercial ammonium carbonate always contains ammonium hydrogen carbonate (ammonium bicarbonate) NH_4HCO_3 and ammonium carbamate $\text{NH}_2\text{COONH}_4$. These impurities form soluble salts with group IV cations, therefore heating at $60\text{-}70^\circ\text{C}$ is necessary to convert these salts to the insoluble carbonates



(3) The alkaline earth carbonates are readily soluble in acidic solutions, so acetic acid could be used to dissolve the

carbonates before adding potassium chromate solution but actually acetate buffer (acetic acid/ammonium acetate) is used to control the acidity at pH 4-5 so that only BaCrO₄ is precipitated, this is because of the alkaline earth chromates barium chromate is the least soluble and calcium chromate is the most soluble. The concentration of chromate ion can be easily regulated through controlling the [H⁺] so that in the buffer system BaCrO₄ precipitates leaving Sr²⁺ and Ca²⁺ in solution. But if [H⁺] is greatly increased (pH < 4), as by adding a strong acid, barium chromate will dissolve.



(CrO₄²⁻ and Cr₂O₇²⁻ are interchangeable depending upon the pH of the medium).

If the solution is not acidic enough (pH > 5) strontium may be partially precipitated.

(4) Alkalinization with NH₄OH is necessary before the addition of (NH₄)₂CO₃ to prevent its decomposition in acidic medium as the reagent is decomposed by acids with the formation of CO₂. In this step Na₂CO₃ can also be used as the centrifugate containing group V cations has been already removed in a

previous step and thus there is no need to control (CO_3^{2-}) by common ion effect.

(5) The excess potassium chromate has to be removed otherwise it will react with triethanolamine giving a dark color which makes the observation of the SrSO_4 and CaC_2O_4 precipitates difficult in the later tests.

(6) Since group IV cations are difficult to separate, masking agents may be used. In order to separate Ca^{2+} and Sr^{2+} sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) or triethanolamine $\text{N}(\text{C}_2\text{H}_5\text{OH})_3$ can be used as they form more stable complexes with Ca^{2+} than with Sr^{2+} , under these conditions, SrSO_4 precipitates but CaSO_4 does not.

(7) The SrSO_4 precipitate and filter paper (cellulose) are charred together where SrSO_4 is reduced to SrS that dissolves in conc. HCl .

Reactions of Group IV cations

- The atoms of barium, strontium and calcium have two valence electrons which are easily lost to form cations with an oxidation state of +2.
- Their salts are normally white powders and form colorless solution unless the anion is colored.

- Solid calcium chloride is hygroscopic and is used as a drying agent.

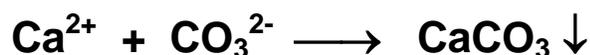
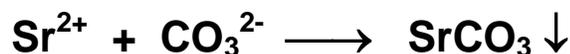
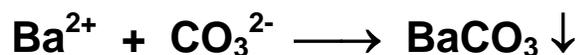
1- Ammonia solution:

No precipitates are formed because of their relatively high solubility. If the alkaline solutions are exposed to the atmosphere, some carbon dioxide is absorbed and a turbidity appears due to carbonate formation. So if a slight turbidity occurs on adding ammonia solution this may be due to small amounts of ammonium carbonate often present in an aged reagent.

Generally, the hydroxides of the three elements of group IV may be considered as completely ionized in aqueous solutions.

2- Ammonium carbonate solution:

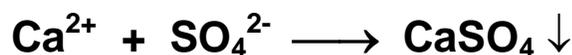
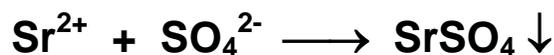
White precipitates of carbonate are formed



The precipitates are soluble in acetic acid and in dilute mineral acids and slightly soluble in solutions of ammonium salts of strong acids.

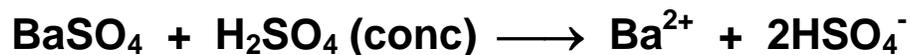
3- Dilute sulphuric acid:

White precipitates are formed.

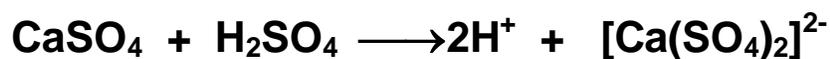


- Of the sulphates of alkaline earth metals, barium sulphate is the most insoluble and calcium sulphate is the most soluble. The solubilities of BaSO_4 and SrSO_4 are so close that the separation of Ba^{2+} and Sr^{2+} ions by adding a soluble sulphate is impractical. But separation of SrSO_4 from CaSO_4 is possible especially on adding $\text{Na}_2\text{S}_2\text{O}_3$ or triethanolamine to decrease the concentration of Ca^{2+} ion through complex formation. As the stability of the complexes increases with increased charge density, thus the complexes of Ca^{2+} ion are more stable than those of Sr^{2+} .
- The solubility of the alkaline earth metal sulphates is slightly increased by the addition of strong acids. The more soluble the metal sulphate, the greater is its increase in solubility on addition of a strong acid. Thus, while the solubility of BaSO_4 is only slightly greater in acidic solution than in water, the solubility of CaSO_4 is greatly enhanced.

- BaSO_4 is almost insoluble in dilute acids and in ammonium sulphate solution but appreciably soluble in boiling concentrated sulphuric acid.



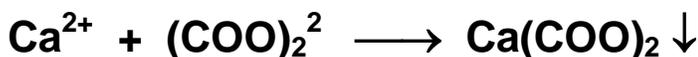
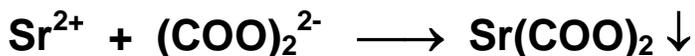
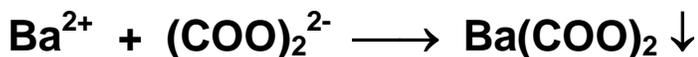
- SrSO_4 is insoluble in ammonium sulphate even on boiling.
- CaSO_4 dissolves in hot concentrated sulphuric acid .



The same complex is formed on heating with ammonium sulphate.

4- Ammonium oxalate solution:

White precipitates are formed.



Calcium oxalate is the least soluble of the alkaline earth metal oxalates. Since oxalic acid is a moderately weak acid, the alkaline earth oxalates are dissolved by solutions of strong acids.

- Barium oxalate is readily dissolved by acetic acid, strontium oxalate is sparingly soluble in it and calcium oxalate is insoluble in it.

5- Saturated calcium sulphate solution:

- Barium gives an immediate white precipitate of barium sulphate.



- Strontium gives a white precipitate of strontium sulphate, formed slowly on cold but more rapidly on boiling (distinction from barium).
- With calcium ions no precipitate is formed (difference from barium and strontium).

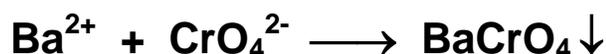
6- Potassium chromate solution:

Of the alkaline earth chromates, barium chromate is the least soluble and calcium chromate is the most soluble.

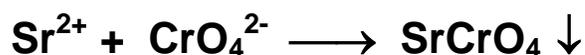
The concentration of the chromate ion can be regulated through control of $[H^+]$ so that in an acetic acid - ammonium acetate buffered solution (pH 4-5), only $BaCrO_4$ precipitates on adding an alkali chromate leaving Sr^{2+} and Ca^{2+} ions in solution. But if $[H^+]$ is greatly increased, as by using a strong acid, barium chromate will dissolve and the solution becomes reddish-orange owing to the formation of dichromate.



- The solubility products for $SrCrO_4$ and $CaCrO_4$ are much larger than for $BaCrO_4$ and hence they require a larger $[CrO_4^{2-}]$ ion concentration to precipitate them. The addition of the buffer system lowers the chromate ion concentration sufficiently to prevent the precipitation of $SrCrO_4$ and $CaCrO_4$ but keeps it high enough to precipitate $BaCrO_4$.
- Barium chromate (yellow precipitate) is insoluble in dilute acetic acid (distinction from strontium and calcium) but readily soluble in mineral acids.



- Strontium chromate (yellow precipitate) is soluble in acetic acid (distinction from barium) and in mineral acids.



- Calcium forms no precipitate with potassium chromate solution neither from dilute solutions nor from concentrated solutions in the presence of acetic acid.

7- Flame test: (Dry test)

Flame tests are used for the detection and confirmation of cations of this group. The alkaline earth elements have loosely bound valence electrons that are capable of being excited even at the low temperature of a Bunsen flame, with emission of visible light. In the flame, volatile salts evaporate and dissociate into ions. The color of the emitted light is characteristic of the element involved.

A platinum wire free from any adhering substances that will color the flame is used for the flame test. The platinum wire is moistened with concentrated hydrochloric acid before being

dipped into the substance. The best flames are obtained with the more volatile halides.

Volatile barium salts, when heated in a non-luminous Bunsen flame impart an apple-green (yellowish-green) color to the flame, strontium salts a crimson and calcium salts a brick red color.