



Anions analysis

The qualitative analysis, or identification, of the common anions is simpler than the analysis of the cations and usually depends on spot tests of the anions rather than separations followed by Confirmatory tests. Nevertheless, for the purpose of systematic qualitative analysis, anions are classified into 3 groups on the basis of their behavior against AgNO_3 and BaCl_2 and the solubility in water and 2M HNO_3 of precipitate products of the reactions.

Group I: anions form white precipitates with both Ag^+ and Ba^{2+} ions slightly soluble in water and soluble in 2M HNO_3 . Group I consists of SO_3^{2-} (sulfite), CO_3^{2-} (carbonate), $\text{C}_2\text{O}_4^{2-}$ (oxalate), $\text{C}_4\text{H}_4\text{O}_6^{2-}$ (tartrate), SO_4^{2-} (sulfate), PO_4^{3-} (phosphate), $\text{S}_2\text{O}_3^{2-}$ (thiosulfate), CrO_4^{2-} (chromate), F^- (fluoride) anions. Group reagent: BaCl_2 in a solution of neutral or slightly alkaline.

Group II anions form insoluble silver salts. Upon the addition of AgNO_3 Cl^- , Br^- , I^- , SCN^- , $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$ ions precipitate as AgCl , AgBr , AgI , $\text{Ag}_4[\text{Fe}(\text{CN})_6]$ and $\text{Ag}_3[\text{Fe}(\text{CN})_6]$ insoluble in 2 M HNO_3 . Group reagent: AgNO_3 in the presence of HNO_3 .

Group III: anions do not form any precipitates with Ag^+ and Ba^{2+} ions. This group consists of NO_3^- (nitric) and NO_2^- (nitrite), CH_3COO^- (acetate) anions.

Group I:

SO_3^{2-}

- $2\text{Ag}^+ + \text{SO}_3^{2-} \rightarrow \text{Ag}_2\text{SO}_3 \downarrow$ white precipitate, soluble in excess SO_3^{2-}
 Ag_2SO_3 is soluble in HNO_3 , CH_3COOH , and HN_3 aq
 Ag_2SO_3 heated with water decomposes into metallic silver and H_2SO_4
 $\text{Ag}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{Ag}^0 + \text{H}_2\text{SO}_4$
- $\text{Ba}^{2+} + \text{SO}_3^{2-} \rightarrow \text{BaSO}_3 \downarrow$ white precipitate, soluble in excess SO_3^{2-}
 BaSO_3 - soluble in diluted HNO_3 with SO_2 liberated; after boiling a white precipitate precipitates BaSO_4
- $\text{Sr}^{2+} + \text{SO}_3^{2-} \rightarrow \text{SrSO}_3 \downarrow$ white precipitate insoluble in CH_3COOH
- $2\text{MnO}_4^- + 5\text{SO}_3^{2-} + 6\text{H}^+ \rightarrow 5\text{SO}_4^{2-} + 2\text{Mn}^{2+} + 3\text{H}_2\text{O}$
turns acidified aqueous KMnO_4 from purple to colourless
- SO_2 liberated on warming with diluted acids:
 $\text{SO}_3^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{SO}_3 \rightarrow \text{SO}_2 \uparrow + \text{H}_2\text{O}$





CO_3^{2-}

1. $2\text{Ag}^+ + \text{CO}_3^{2-} \rightarrow \text{Ag}_2\text{CO}_3\downarrow$ white precipitate, soluble in dilute HNO_3 , CH_3COOH and NH_3 aq; after heating, it decomposes into Ag_2O (brown precipitate) and CO_2
 $\text{Ag}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{Ag}_2\text{O}\downarrow + \text{CO}_2\uparrow$
2. $\text{Ba}^{2+} + \text{CO}_3^{2-} \rightarrow \text{BaCO}_3\downarrow$ white precipitate, soluble in diluted mineral acids (except H_2SO_4) and CH_3COOH
3. CO_2 liberated by diluted acids:
4. $\text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{CO}_2\uparrow + \text{H}_2\text{O}$
 CO_2 gives a white precipitate with limewater ($\text{Ca}(\text{OH})_2$) (precipitate dissolves with excess CO_2)

$\text{C}_2\text{O}_4^{2-}$

1. $2\text{Ag}^+ + \text{C}_2\text{O}_4^{2-} \rightarrow \text{Ag}_2\text{C}_2\text{O}_4\downarrow$ white cheese sediment, soluble in diluted HNO_3 and NH_3 aq
2. $\text{Ba}^{2+} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{BaC}_2\text{O}_4\downarrow$ white precipitate, soluble in diluted HNO_3 and NH_3 aq
3. $\text{Ca}^{2+} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{CaC}_2\text{O}_4\downarrow$ white precipitate, soluble in mineral acids, CH_3COOH and in excess $\text{C}_2\text{O}_4^{2-}$
4. $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 10 \text{CO}_2\uparrow + \text{Mn}^{2+} + 8\text{H}_2\text{O}$, turns from purple to colourless, CO_2 liberated

$\text{S}_2\text{O}_3^{2-}$

1. $\text{Ag}^+ + \text{S}_2\text{O}_3^{2-} \rightarrow \text{Ag}_2\text{S}_2\text{O}_3\downarrow$ white fast yellowing and then blackening precipitate, soluble in excess $\text{S}_2\text{O}_3^{2-}$
 $\text{Ag}_2\text{S}_2\text{O}_3 + 3\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$
2. $\text{Ba}^{2+} + \text{S}_2\text{O}_3^{2-} \rightarrow \text{BaS}_2\text{O}_3\downarrow$ white precipitate, soluble in hot water and diluted HCl and HNO_3
3. $\text{Fe}^{3+} + 2\text{S}_2\text{O}_3^{2-} \rightarrow \text{Fe}(\text{S}_2\text{O}_3)_2^{2-}$ unstable purple compound, decomposing with formation $\text{S}_2\text{O}_6^{2-}$
4. Acids decompose $\text{S}_2\text{O}_3^{2-}$ to SO_2 and S^0 . The reaction can be accelerated by heating:
 $\text{S}_2\text{O}_3^{2-} + \text{H}^+ \rightarrow \text{S} + \text{SO}_2 + \text{H}_2\text{O}$





CrO_4^{2-}

1. $2\text{Ag}^+ + \text{CrO}_4^{2-} \rightarrow \text{Ag}_2\text{CrO}_4 \downarrow$ brownish red precipitate, soluble in diluted HNO_3 and NH_3 aq, insoluble in CH_3COOH
2. $\text{Ba}^{2+} + \text{CrO}_4^{2-} \rightarrow \text{BaCrO}_4 \downarrow$ yellow precipitate, soluble in diluted HNO_3 and HCl , insoluble in CH_3COOH
3. $\text{Pb}^{2+} + \text{CrO}_4^{2-} \rightarrow \text{PbCrO}_4 \downarrow$ yellow precipitate, soluble in diluted HNO_3 and bases
4. $\text{Hg}_2^{2+} + \text{CrO}_4^{2-} \rightarrow \text{Hg}_2\text{CrO}_4 \downarrow$ brown amorphous precipitate, during cooking it changes into a crystalline bright red precipitate
5. CrO_4^{2-} reduces to Cr^{3+} (green solution)

PO_4^{3-}

1. $3\text{Ag}^+ + 2\text{HPO}_4^{2-} \rightarrow \text{Ag}_3\text{PO}_4 \downarrow + \text{H}_2\text{PO}_4^-$ yellow precipitate, soluble in diluted HNO_3 , CH_3COOH and NH_3 aq
2. $\text{Ba}^{2+} + \text{HPO}_4^{2-} \rightarrow \text{BaHPO}_4 \downarrow$ white precipitate, soluble in diluted HNO_3 , HCl and CH_3COOH

SO_4^{2-}

1. $\text{Ba}^{2+} + \text{SO}_4^{2-} \rightarrow \text{BaSO}_4 \downarrow$ white precipitate, insoluble in diluted HNO_3 and HCl
2. $\text{Pb}^{2+} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 \downarrow$ white precipitate, soluble in concentrated KOH and H_2SO_4
3. $\text{Cu}^0 + \text{SO}_4^{2-} + 4\text{H}^+ \rightarrow \text{SO}_2 \uparrow + \text{Cu}^{2+} + \text{H}_2\text{O}$

The same reaction as with Cu occurs with H_2S , HJ , HBr

F^-

1. $\text{Ba}^{2+} + 2\text{F}^- \rightarrow \text{BaF}_2 \downarrow$ white precipitate
2. $\text{Pb}^{2+} + 2\text{F}^- \rightarrow \text{PbF}_2 \downarrow$ white precipitate
3. $\text{Fe}(\text{SCN})^{2+} + 6\text{F}^- + \text{H}^+ = \text{FeF}_6^{3-} + 2\text{SCN}^-$ discoloration of the solution

