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), $C_2O_4^{2-}$ (oxalate), $C_4H_4O_6^{2-}$ (tartrate), SO_4^{2-} (sulfate), PO_4^{3-} (phosphate), $S_2O_3^{2-}$ (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^-, $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$ ions precipitate as AgCl, AgBr, AgI, $Ag_4[Fe(CN)_6]$ and $Ag_3[Fe(CN)_6]$ 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-}

1. $2Ag^+ + SO_3^{2-} \rightarrow Ag_2SO_3 \downarrow$ 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
   $Ag_2SO_3 + H_2O \rightarrow Ag^0 + H_2SO_4$
2. $Ba^{2+} + SO_3^{2-} \rightarrow BaSO3\downarrow$ 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 $BaSO_4$
3. $Sr^{2+} + SO_3^{2-} \rightarrow SrSO_3\downarrow$ white precipitate insoluble in CH_3COOH
4. $2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 3H_2O$
   turns acidified aqueous $KMnO_4$ from purple to colourless
5. SO_2 liberated on warming with diluted acids:
   $SO_3^{2-} + 2H^+ \rightarrow H_2SO_3 \rightarrow SO_2\uparrow + H_2O$

CO_3^{2-}

1. $2Ag^+ + CO_3^{2-} \rightarrow Ag_2CO_3\downarrow$ 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
   $Ag_2CO_3 + H_2O \rightarrow Ag_2O\downarrow + CO_2\uparrow$
2. $Ba^{2+} + CO_3^{2-} \rightarrow BaCO_3\downarrow$ white precipitate, soluble in diluted mineral acids (except H_2SO_4) and CH_3COOH
3. CO_2 liberated by diluted acids:
4. $CO_3^{2-} + 2H^+ \rightarrow H_2CO_3 \rightarrow CO_2\uparrow + H_2O$
   CO_2 gives a white precipitate with limewater ($Ca(OH)_2$) (precipitate dissolves with excess CO_2)

$C_2O_4^{2-}$

1. $2Ag^+ + C_2O_4^{2-} \rightarrow Ag_2C_2O_4\downarrow$ white cheese sediment, soluble in diluted HNO_3 and NH_3aq
2. $Ba^{2+} + C_2O_4^{2-} \rightarrow BaC_2O4\downarrow$ white precipitate, soluble in diluted HNO_3 and NH_3aq
3. $Ca^{2+} + C_2O_4^{2-} \rightarrow CaC_2O_4\downarrow$ white precipitate , soluble in mineral acids, CH_3COOH and in excess $C_2O_4^{2-}$
4. $2MnO^{4-} + 5C_2O_4^{2-} + 16H^+ \rightarrow 10\ CO_2\uparrow + Mn^{2+} + 8H_2O$, turns from purple to colourless, CO_2 liberated

$S_2O_3^{2-}$

1. $Ag^+ + S_2O_3^{2-} \rightarrow Ag_2S_2O_3\downarrow$ white fast yellowing and then blackening precipitate, soluble in excess $S_2O_3^{2-}$
   $Ag_2S_2O_3 + 3S_2O_3^{2-} \rightarrow 2Ag(S_2O_3)_2^{3-}$
2. $Ba^{2+} + S_2O_3^{2-} \rightarrow BaS_2O_3\downarrow$ white precipitate, soluble in hot water and diluted HCl and HNO_3
3. $Fe^{3+} + 2S_2O_3^{2-} \rightarrow Fe(S_2O_3)^{2-}$ unstable purple compound, decomposing with formation $S_2O_6^{2-}$
4. Acids decompose $S_2O_3^{2-}$ to SO_2 and S^0. The reaction can be accelerated by heating:
   $S_2O_3^{2-} + H^+ \rightarrow S + SO_2 + H_2O$

CrO_4^-

1. $2Ag^+ + CrO_4^- \rightarrow Ag_2CrO_4\downarrow$ brownish red precipitate, soluble in diluted HNO_3 and NH_3 aq, insoluble in CH_3COOH
2. $Ba^{2+} + CrO_4^{2-} \rightarrow BaCrO_4\downarrow$ yellow precipitate, soluble in diluted HNO_3 and HCl, insoluble in CH_3COOH
3. $Pb^{2+} + CrO_4^{2-} \rightarrow PbCrO_4\downarrow$ yellow precipitate, soluble in diluted HNO_3 and bases
4. $Hg_2^{2+} + CrO_4^{2-} \rightarrow Hg_2CrO_4\downarrow$ 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. $3Ag^+ + 2HPO_4^{2-} \rightarrow Ag_3PO_4\downarrow + H_2PO_4^-$ yellow precipitate, soluble in diluted HNO_3, CH_3COOH and NH_3 aq
2. $Ba^{2+} + HPO_4^{2-} \rightarrow BaHPO_4\downarrow$ white precipitate, soluble in diluted HNO_3, HCl and CH_3COOH

SO_4^{2-}

1. $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4\downarrow$ white precipitate, insoluble in diluted HNO_3 and HCl
2. $Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4\downarrow$ white precipitate, soluble in concentrated KOH and H_2SO_4
3. $Cu^0 + SO_4^{2-} + 4H^+ \rightarrow SO_2\uparrow + Cu^{2+} + H_2O$

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

F^-

1. $Ba^{2+} + 2F^- \rightarrow BaF_2\downarrow$ white precipitate
2. $Pb^{2+} + 2F^- \rightarrow PbF_2\downarrow$ white precipitate
3. $Fe(SCN)^{2+} + 6F^- + H^+ = FeF_6^{3-} + 2SCN^-$ discoloration of the solution