Introduction

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 7 groups on the basis of their behaviour 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 precipitate of silver salts which are insoluble in water and 2M HNO_3 solution. Barium salts are soluble in water. Group I consists of Cl^- (chloride), Br^-(bromide), I^-(iodide), $[Fe(CN)_6]^{4-}$ (ferrocyanide), $[Fe(CN)_6]^{3-}$ (ferricyanide) anions.

Group II: anions form white precipitates of Ag salts which are slightly soluble in water and soluble in 2M HNO_3 solution. Barium salts are soluble in water. Group II consists of NO_2^- (nitrite), CH_3COO^- (actetate), S^{2-} (sulfide).

Group III: anions form white precipitates with both Ag^+ and Ba^{2+} ions slightly soluble in water and soluble in 2M HNO_3. Group III consists of SO_3^{2-} (sulfite), CO_3^{2-} (carbonate), $C_2O_4^{2-}$ (oxalate), BO_3^{3-} (borate), $C_4H_4O_6^{2-}$ (tartrate) anions.

Group IV: anions form color precipitates with Ag^+ and Ba^{2+} ions which are slightly soluble in water and soluble in 2M HNO_3 solution. Group IV contain PO_4^{3-} (phosphate), $S_2O_3^{2-}$ (thiosulfate), CrO_4^{2-} (chromate) anions.

Group V: anions do not form any precipitates with Ag^+ and Ba^{2+} ions. This group consists of NO_3^- (nitric) and MnO_4^- (permanganate) anions.

Group VI: SO_4^{2-} ions form Ag_2SO_4 precipitate soluble in water and white precipitate of $BaSO_4$ insoluble in water and 2M HNO_3.

Exercise 1:

Introduction

Group I anions form insoluble silver salts. Upon the addition of $AgNO_3$ Cl^-, Br^-, I^-, $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$ ions precipitate as AgCl, AgBr, AgI, $Ag_4[Fe(CN)_6]$ and $Ag_3[Fe(CN)_6]$ insoluble in 2 M HNO_3

Separation and identification of I Group anions Cl^-, Br^-, I^-, $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$

The initial sample may be colorless or yellow. If the sample is yellow it may contain at least one of $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ ions. Therefore, they must be identified as first from the initial sample with the following reactions:

$[Fe(CN)_6]^{4-}$

$K_4[Fe(CN)_6 + FeCl_{3\,excess} \rightarrow Fe_4[Fe(CN)_6]\downarrow + 12\,KCl$ reactions 1-2

Prussian blue - a dark blue pigment

$K_4[Fe(CN)_6 + FeSO_4 \rightarrow K_2Fe[Fe(CN)_6]\downarrow + K_2SO_4$
reaction 2

light blue color which changes into dark blue

$[Fe(CN)_6]^{3-}$

$K_3[Fe(CN)_6 + FeCl_2 \rightarrow KFe[Fe(CN)_6]\downarrow + 2\ KCl$
$KFe[Fe(CN)_6]\downarrow + FeCl_2 \rightarrow FeFe_2[Fe(CN)_6]_2\downarrow$ — reactions 3-4
blue precipitate – **Turnbull blue**

$K_3[Fe(CN)_6 + FeCl_3 \rightarrow Fe^{III}[Fe^{II}(CN)_6] + 3\ KCl$ — reaction 5
dark-brown color

After identification of these anions they have to be removed before further identification of the rest of anions of this group. For this purpose the excess of $ZnSO_4$ solution should be used, because $ZnSO_4$ reacts with $[Fe(CN)_6]^{4-}$and $[Fe(CN)_6]^{4-}$ anions and precipitates as zinc salts of $Zn_2[Fe(CN)_6]$ and $Zn_3[Fe(CN)_6]$:

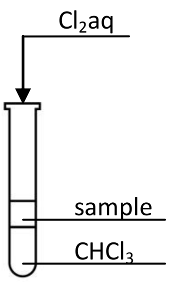
$ZnSO_4 + K_4Fe(CN)_6 \rightarrow Zn_2[Fe(CN)_6]\downarrow + 2\ K_2SO_4$ <u>white precipitate</u> — reaction 6

$ZnSO_4 + K_3Fe(CN)_6 \rightarrow Zn_3[Fe(CN)_6]\downarrow + 3\ K_2SO_4$ <u>orange precipitate</u> — reaction 7

When precipitates occurred, filtrate the mixture and discard the precipitate A (scheme 1). Filtrate A contains only Cl^-, Br^- and I^- and should be colorless. If the Filtrate A is still yellow, additional portion of $ZnSO_4$ must be added and resulted precipitate filtrated again. Then the rest of anions can be identified from obtained Filtrate A.

Br^- and I^- ions can be also identified from the initial sample. The identification of these two ions can be followed in one test tube with the use of Cl_2aq and $CHCl_3$. For this purpose take 2 ml of the initial sample, add 2 ml of $CHCl_3$ and some portion of Cl_2aq solution. Next, close test tube with your thumb and shake it vigorously. The presence of I^- ions is confirmed, when the organic layer of $CHCl_3$ is tinted violet.

$2NaI + Cl_2aq \rightarrow 2NaCl + I_2$ — reaction 8



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The chlorine water should be added several time with small portions in order to check the presence of Br^-. When the violet color will disappear from the chloroform layer and yellow-orange color will appear we can state, that Br^- ions are present in our initial sample.

$2NaBr + Cl_2aq \rightarrow 2NaCl + Br_2$ — reaction 9

The lack of the color allow to state that Br^- ions are not present in the analyzed sample.

NOTE: I^- and $[Fe(CN)_6]^{3-}$ ions cannot be present together in one solution, because I^- ions undergo the oxidation in the presence of $[Fe(CN)_6]^{3-}$ ions.

$2\ K_3[Fe(CN)_6]\ +\ 2\ KI \rightarrow I_2\ +\ 2\ K_4[Fe(CN)_6$ reaction 10

Chloride ions Cl^- can be identified from initial sample. As first silver nitrate $AgNO_3$ and 2 M HNO_3 must be added. All anions from I group will precipitate as silver salts.

$NaCl\ +\ AgNO_3 \rightarrow AgCl\downarrow\ +\ NaNO_3$ reaction 11

$NaBr\ +\ AgNO_3 \rightarrow AgBr\downarrow\ +\ NaNO_3$ reaction 12

$NaI\ +\ AgNO_3 \rightarrow AgI\downarrow\ +\ NaNO_3$ reaction 13

Silver chloride is insoluble in diluted inorganic acids and dissolves in diluted NH_3aq solution (*1 portion of NH_3aq solution and 3 portions of distilled H_2O*):

$AgCl\ +\ 2\ NH_3 \rightarrow Ag(NH_3)_2Cl$ reaction 14

After adding HNO_3 solution to resulting Filtrate C (scheme 1) white precipitate of AgCl is obtained again:

$Ag(NH_3)_2Cl\ +\ HNO_3 \rightarrow AgCl\downarrow + NH_4NO_3$ reaction 15

The rest of analytical reactions of Cl^-, Br^-, I^-, $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$ ions

H_2SO_4 diluted
Cl^- no reaction
Br^- and I^- react in higher temperature
$NaBr +\ H_2SO_4 \rightarrow HBr\ +\ NaHSO_4$
$NaI +\ H_2SO_4 \rightarrow HI\ +\ NaHSO_4$
$2\ K_4[Fe(CN)_6]\ +\ 3\ H_2SO_4 \rightarrow K_2Fe[Fe(CN)_6]\downarrow\ +\ 3\ K_2SO_4\ +\ 6\ HCN$ at room temperature

$KMnO_4$ in acidic solution
Cl^- no reaction in cold solution, but Cl^- undergo reduction after heating
$10\ KCl\ +\ 2\ KMnO_4\ +\ 8\ H_2SO_4 \rightarrow 5\ Cl_2\ +\ 2\ MnSO_4\ +\ 6\ K_2SO_4\ +\ 8\ H_2O$

Br^-, I^- and $[Fe(CN)_6]^{4-}$ undergo reduction at lower temperature
$10\ KBr\ +\ 2\ KMnO_4\ +\ 8\ H_2SO_4 \rightarrow 5\ Br_2\ +\ 2\ MnSO_4\ +\ 6\ K_2SO_4\ +\ 8\ H_2O$
(and similarly for I^-)
$KMnO_4\ +\ 5\ K_4[Fe(CN)_6]\ +\ 4\ H_2SO_4 \rightarrow 5\ K_3[Fe(CN)_6]\ +\ MnSO_4\ +\ 3\ K_2SO_4\ +\ 4\ H_2O$

Cu(II) salts
Cu(II) salts undergo reduction in the presence of I^- ions and form CuI slightly soluble in water
$2\ CuSO_4\ +\ 4\ KI \rightarrow 2\ CuI\downarrow\ +\ I_2\ +\ 2\ K_2SO_4$

Hydrogen peroxide H_2O_2

Iodide ions undergo oxidation in the presence of H_2O_2 in the presence of weak acetic acid

$2\ KI + H_2O_2 + 2\ CH_3COOH \rightarrow I_2 + 2\ CH_3COOK + 2\ H_2O$

Fe(III) salts

$FeCl_3$ evolve gasous I_2 from I^- ions solution

$2\ FeCl_3 + 2\ KI \rightarrow FeCl_2 + I_2 + 2\ KCl$

$K_4[Fe(CN)_6 + FeCl_{3\ excess} \rightarrow Fe_4[Fe(CN)_6]\downarrow + 12\ KCl$

Prussian blue - a dark blue pigment

$K_3[Fe(CN)_6] + FeCl_3 \rightarrow Fe^{III}[Fe^{II}(CN)_6] + 3\ KCl$

Potassium dichromate $K_2Cr_2O_7$

causes the oxidation of Br^- and I^- in the presence of sulfuric acid H_2SO_4

$K_2Cr_2O_7 + 6\ KBr + 7\ H_2SO_4 \rightarrow 3\ Br_2 + 4\ K_2SO_4 + Cr_2(SO_4)_3 + 7\ H_2O$

$K_2Cr_2O_7 + 6\ K_4[Fe(CN)_6] + 7\ H_2SO_4 \rightarrow 6\ K_3[Fe(CN)_6] + Cr_2(SO_4)_3 + 4\ K_2SO_4 + 7\ H_2O$

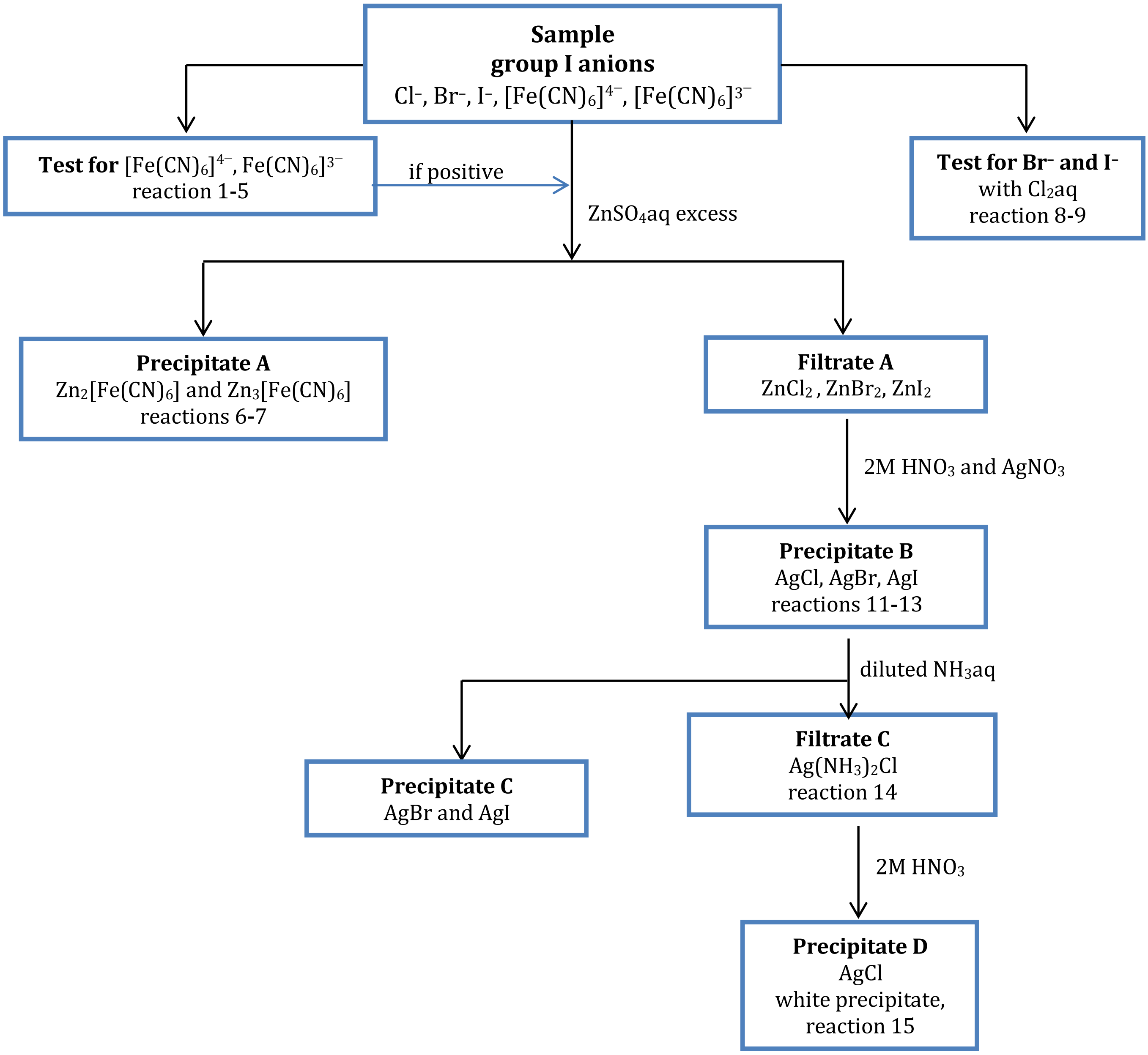
Other reducing agents in reactions with $[Fe(CN)_6]^{3-}$ ions:

$2\ K_3[Fe(CN)_6] + 2\ KI \rightarrow I_2 + 2\ K_4[Fe(CN)_6]$

$2\ K_3[Fe(CN)_6] + K_2S \rightarrow 2\ K_4[Fe(CN)_6] + S$

$K_3[Fe(CN)_6] + Fe(OH)_2 + KOH \rightarrow K_4[Fe(CN)_6] + Fe(OH)_3$

Scheme 1


Sample
group I anions
Cl⁻, Br⁻, I⁻, [Fe(CN)6]4−, [Fe(CN)6]3−
Test for [Fe(CN)6]4−, Fe(CN)6]3−
reaction 1-5
if positive
ZnSO4aq excess
Test for Br⁻ and I⁻
with Cl2aq
reaction 8-9
Precipitate A
Zn2[Fe(CN)6] and Zn3[Fe(CN)6]
reactions 6-7
Filtrate A
ZnCl2 , ZnBr2, ZnI2
2M HNO3 and AgNO3
Precipitate B
AgCl, AgBr, AgI
reactions 11-13
diluted NH3aq
Precipitate C
AgBr and AgI
Filtrate C
Ag(NH3)2Cl
reaction 14
2M HNO3
Precipitate D
AgCl
white precipitate,
reaction 15