The goal of the Exercise 8 is to analyze a solution that may contain the following anions: PO_4^{3-}, $S_2O_3^{2-}$, CrO_4^{2-} and SO_4^{2-}. These anions form white or colored precipitates with $AgNO_3$ and white precipitates with $BaCl_2$. For the analytical reactions Na_2HPO_4 salt is used as a source of PO_4^{3-} anions.

Analytical reactions of phosphate(V) ions PO_4^{3-}

1. $AgNO_3$ gives yellow precipitate of silver phosphate:

$$Na_2HPO_4 + 3\ AgNO_3 = Ag_3PO_4\downarrow + 2\ NaNO_3 + HNO_3$$

which dissolves in mineral acids, acetic acid and ammonia.

2. $BaCl_2$ precipitates white residue of barium hydrogen phosphate which dissolves in acetic acid, ammonia, HNO_3 and HCl:

$$Na_2HPO_4 + BaCl_2 = BaHPO_4\downarrow + 2\ NaCl$$

3. Magnesia mixture

This mixture is composed of magnesium chloride, ammonium chloride and ammonia and allow to identify the HPO_4^{2-} ions even in very diluted solutions as a white precipitate of $MgNH_4PO_4$ salt :

$$HPO_4^{2-} + NH_3{\cdot}H_2O + MgCl_2 + 5\ H_2O = MgNH_4PO_4{\cdot}6H_2O\downarrow + 2\ Cl^-$$

Analytical reactions of chromate ions CrO_4^{2-}

1. $AgNO_3$ gives red-brownish precipitate of silver chromate which dissolves easily in diluted HNO_3, and ammonia:

$$2\ AgNO_3 + Na_2CrO_4 = Ag_2CrO_4\downarrow + 2\ NaNO_3$$

2. $BaCl_2$ precipitates yellow residue of $BaCrO_4$ which dissolves in mineral acids beside H_2SO_4. It also does not dissolve in CH_3COOH

$$BaCl_2 + Na_2CrO_4 = BaCrO_4\downarrow + 2\ NaCl$$

3. H_2SO_4 acid converts chromates into dichromates and the color of the solution changes from yellow to orange:

$$2\ Na_2CrO_4 + H_2SO_4 = Na_2SO_4 + Na_2Cr_4O_7 + H_2O$$

4. $Pb(CH_3COO)_2$ precipitates chromate and dichromate ions as yellow precipitate of lead(II) chromate according to the reaction:

$$Pb(CH_3COO)_2 + K_2CrO_4 = PbCrO_4\downarrow + 2\ CH_3COOK$$

5. Reducing agents: like Zn_{metal}, H_2S, Br^-, Fe^{2+} are oxidized by dichromates in acidic solution:

$$K_2Cr_2O_7 + 3\ Zn + 7\ H_2SO_4 = Cr_2(SO_4)_3 + 3\ ZnSO_4 + K_2SO_4 + 7\ H_2O$$
$$K_2Cr_2O_7 + 3\ H_2S + 4\ H_2SO_4 = Cr_2(SO_4)_3 + 3\ S + K_2SO_4 + 7\ H_2O$$
$$K_2Cr_2O_7 + 6\ FeSO_4 + 7\ H_2SO_4 = Cr_2(SO_4)_3 + 3\ Fe_2(SO_4)_3 + K_2SO_4 + 7\ H_2O$$
$$K_2Cr_2O_7 + 6\ KBr + 7\ H_2SO_4 = Cr_2(SO_4)_3 + 3\ Br_2 + 4\ K_2SO_4 + 7\ H_2O$$
$$K_2Cr_2O_7 + 3\ H_2C_2O_4 + 4\ H_2SO_4 = Cr_2(SO_4)_3 + 6\ CO_2 + K_2SO_4 + 7\ H_2O$$
$$K_2Cr_2O_7 + CH_3CH_2OH + 8\ HNO_3 = 2\ Cr(NO_3)_3 + 3\ CH_3CHO + 2\ KNO_3 + 7\ H_2O$$

$$K_2Cr_2O_7 + 14\ HCl = 2\ KCl + 2\ CrCl_3 + 3\ Cl_2 + 7\ H_2O$$

In neutral pH of the solution:

$$K_2Cr_2O_7 + 3\ H_2S + H_2O = 2\ Cr(OH)_3\downarrow + 3\ S\downarrow + 2\ KOH$$

Analytical reactions of thiosulphate ions $S_2O_3^{2-}$

1. **$AgNO_3$** added in excess precipitates white residue of silver thiosulphate. $Ag_2S_2O_3$ is not stable in water solution and its color changes in time. $Ag_2S_2O_3$ disproportionates to give silver sulphide (black precipitate) and sulphuric acid. That is, a white precipitate is obtained which changes to brown and finally to black color.

$$Na_2S_2O_3 + 2\ AgNO_3 + Ag_2S_2O_3\downarrow + 2\ NaNO_3$$
$$Ag_2S_2O_3 + H_2O = Ag_2S\downarrow + H_2SO_4$$

2. **$BaCl_2$** also precipitates as white residue of barium thiosulphate:

$$Ba^{2+} + S_2O_3^{2-} = BaS_2O_3\downarrow$$

soluble in hot water and diluted HCl and HNO_3

3. **I_2** is reduced into iodides, whereas thiosulphates are oxidized into tetrathionates (reaction used in iodometry):

$$2\ Na_2S_2O_3 + I_2 = 2\ NaI + Na_2S_4O_6$$

4. **Fe(III) salts** form soluble salts of Fe(II)

$$2\ FeCl_3 + 2\ Na_2S_2O_3 = 2\ FeCl_2 + Na_2S_4O_6 + 2\ NaCl$$

5. **Cl_{2aq} and Br_{2aq}** are reduced into chlorides and bromides:

$$Na_2S_2O_3 + 4\ Cl_2 + 5\ H_2O = Na_2SO_4 + H_2SO_4 + 8\ HCl$$

6. **$KMnO_4$ (and dichromates $Cr_2O_7^{2-}$)** oxidizes thiosulphates into sulphates:

$$8\ KMnO_4 + 5\ Na_2S_2O_3 + 7\ H_2SO_4 = 8\ MnSO_4 + 5\ Na_2SO_4 + 4\ K_2SO_4 + 7\ H_2O$$
$$4\ K_2Cr_2O_7 + 3\ Na_2S_2O_3 + 13\ H_2SO_4 = 4\ Cr_2(SO_4)_3 + 4\ K_2SO_4 + 3\ Na_2SO_4 + 13\ H_2O$$

7. **H atomic (Zn + HCl)** reduces thiosulphates into hydrogen sulfide in acidic solution:

$$Na_2S_2O_3 + 4\ Zn + 10\ HCl = 2\ H_2S + 4\ ZnCl_2 + 2\ NaCl + 3\ H_2O$$

Analytical reactions of sulphate ions SO_4^{2-}

1. **$AgNO_3$** does not precipitate any residues. Ag_2SO_4 precipitate can be obtained only from very concentrated solutions.

2. **$BaCl_2$** precipitates as white barium sulphate:

$$BaCl_2 + Na_2SO_4 = BaSO_4\downarrow + 2\ NaCl$$

This precipitate dissolves only in concentrated H_2SO_4

$$BaSO_4 + H_2SO_4 = Ba(HSO_4)_2$$

Identification of Groups IV and VI anions in analyzed mixture

Test for CrO_4^{2-} ions:

Water solutions of chromate salts are yellow in general. Therefore, the presence of CrO_4^{2-} ions is quite easy to establish.

NOTE!

$S_2O_3^{2-}$ and CrO_4^{2-} ions cannot exist together in one mixture because in acidic solution these anions react with each other according to the following redox reaction:

$$3\,S_2O_3^{2-} + 8\,CrO_4^{2-} + 34\,H_3O^+ = 6\,SO_4^{2-} + 8\,Cr^{2+} + 51\,H_2O$$

Test for PO_4^{3-} ions:

Prepare a clean test tube and add 2mL of analyzing solution to it. Next, add about 1mL of magnesia mixture (mixture composed of magnesium chloride, ammonium chloride and ammonia). This mixture is ready to use in bottle titled in Polish "MIESZANINA MAGNEZOWA"

$$HPO_4^{2-} + NH_3{\cdot}H_2O + MgCl_2 + 5\,H_2O = MgNH_4PO_4{\cdot}6H_2O\downarrow + 2\,Cl^-$$

The white precipitate of $MgNH_4PO_4{\cdot}6H_2O$ unequivocally prove the presence of PO_4^{3-} ions in analyzed solution.

Test for $S_2O_3^{2-}$ ions:

The absence of CrO_4^{2-} ions in analyzed solution allow to verify the presence of $S_2O_3^{2-}$ with simple test. Take 2 mL of analyzing solution and add small amount of diluted H_2SO_4 acid. Then, add small amount of $KMnO_4$ solution and observe the solution in the test tube. The disappearance of violet color of $KMnO_4$ solution proves the presence of $S_2O_3^{2-}$ anions.

$$8\,KMnO_4 + 5\,Na_2S_2O_3 + 7\,H_2SO_4 = 4\,K_2SO_4 + 8\,MnSO_4 + 5\,Na_2SO_4 + 7\,H_2O$$

Test for SO_4^{2-} ions:

NOTE!

First we must remove $S_2O_3^{2-}$ anions if they are present in analyzed sample. For this, take a clean test tube and add 2mL of analyzed mixture to it. Next, add 1mL of 6 M hydrochloric acid to the tube and shake gently to mix the contents. Thiosulfate ions decompose into solid sulfur and gaseous SO_2 according the reaction:

$$Na_2S_2O_3 + 2\,HCl = S\downarrow + SO_2\uparrow + 2\,NaCl + H_2O$$

The white precipitate of sulfur must be filtered out until the filtrate is limpid. Then, add about 1 mL of barium chloride solution to the tube, shake it gently and observe. The precipitation of white $BaSO_4$ proves the presence of SO_4^{2-} ions in analyzed mixture.

$$BaCl_2 + Na_2SO_4 = BaSO_4\downarrow + 2\,NaCl$$

The end ☺