14th WEEK

- Make-up experiments for Cation and Anion group sample analysis are completed by the students.
- Students return all the departmental laboratory equipments that they were delivered in the begining of the course.
- The students learn how to deal with qualitative analysis of cation and anion mixtures. However, they study these mixtures with less interfering effects of other ions in the solution. They cannot be fully knowledged about details of solutions containing problems with the solubility of solid samples. Therefore, a brief information about carbonate transposition (fusion method) is given and a representative experiment is shown by the assistants.

FUSION METHOD

A chemical analysis usually requires dissolution of the material. For this purpose several solvents are used. First, it is checked whether the material is dissolved in deionized water or not. If it does not dissolved in pure water, organic solvents are tried. Finally, if it is not soluble again, diluted and concentrated acids are used. Moreover, natural materials (stones, rocks), artificial materials (cement, brick) are dissolved by fusion method at high temperature when they are not soluble in above mentioned liquids.

The materials that are used for fusion purposes are called **fusion materials** and the process during the dissolution of solids is named as **fusion method**. Fusion materials are high temperature acids or bases.

Types of fusion methods:

Fusion methods are named according to the fusion materials used in the process. Below are the fusion materials:

1. KHF_2 potassium bifluoride
2. $KHSO_4$ potassium bisulfate
3. Na_2CO_3-S sodium carbonate - sulfur mixture
4. $Na_2B_4O_7$ borax
5. $NaNH_4PO_4$ sodium ammonium phosphate
6. $CaCO_3$-NH_4Cl
7. Peroxide
8. NaOH-KOH
9. Na_2CO_3-KNO_3
10. Na_2CO_3

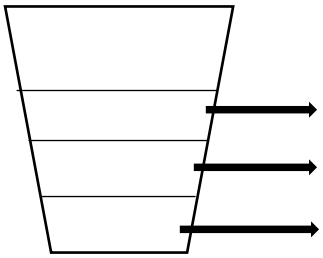
Precautions during fusion process

1. In general, platinum crucible is used for fusion method. However porcelain crucibles are also used for the determination of many cations except for silica.For silica, crucibles made of iron/nickel must be used.
    - NOTE: For Na_2CO_3 and KNO_3fusion methods, there mustn't be any chloride ions in the sample. Because of Cl_2releasing from the reaction, platinum is oxidized which is a very dangerous reaction.
2. Crucibles are exposed to oxidizing flame.
3. Samples must be ground and then mixed with fusion materials homogeneously by using stirring rods.
4. Crucibles must not be filled up to more than half of it.

5. Heating should be done slowly in the beginning, then the temperature should be increased. Sudden increase in temperature causes the splash of material from sample due to the release of the water vapor/gases from the sample.
6. A homogeneous melt should be obtained at the heating step. If the particle remains on the bottom of the crucible, it must be melted at 900^{o}C in high temperature furnace.
7. The melt in the crucible mustn't be left to freeze. It should be rotated with a clean hand tweezers to freeze on the sides of the crucible.
8. After cooling the crucible in the desiccator for a while, the dissolving process should be started.

Preparing Fusion Materials:

Anhydrous sodium carbonate (as an example of fusion material) is weighed as 10 times the mass of fine powdered sample. It is homogeneously groundon a clean dry paper with stirring rod. Then it is separated into three equal amounts. The portions of fusion materials are used as in the figure below:



Fusion steps:

Crucible is rotated at a 45^{o} degree angle when exposed to the low temperature flame of the bunsen burner.The mixture in the crucible melts. The volume of the mixture should be decreased to the¼ of the initial amount of the total material in the crucible. A homogeneous melt should be obtained. If any solid particle remains on the bottom of the crucible, it must be melted at 900^{o}C in high temperature furnace. It takes about 1 hour to melt.
0.2-0.3 g of samples are taken.
The crucible should be rotated with a clean hand tweezers to freeze the melt on the sides of the crucible.
100 mL of distilled water is boiled in a separatebeaker (400 mL). Boiled water is left to cool at ambient temperature.

Cooled crucibles (80-100 ^{o}C) are put into boiled water prepared in step 4. By the help of water, melt can be prevented from being sticked to the sides of the crucible and melt easily distributes in the aqua solution.

The remaining portion of melt is taken out by breaking the crucible in the beaker. Then the water is boiled again to remove the rest of the melt from crucible.

Mixture is filtered with blue band filter paper. Broken fragments of crucible are washed with distilled water into the beaker witha clean hand tweezers.

1 M HCl is added to the filtrate to dissolve the carbonates of other cations and to precipitate Si as gelatinous H_2SiO_3(s).

The new mixture is filtrated by black band filter paper to collect gelatinous H_2SiO_3.

The analysis of cations in a sample is made by precipitating them in the order of;

1. Si, Sn
2. Ba, Pb
3. +3 charged cations
4. +2 charged cations
5. +1 charged cations

Fusion (Na_2CO_3)

Samples are dissolved according to the replacement of cations and anions and oxidation basis at appropriate temperature.

1. Na^+, K^+, NH_4^+carbonates are dissolved in water however carbonates of other cations are not dissolved. Therefore Na_2CO_3 is used as fusion material to convert all materials into carbonate salts. Additionally KNO_3 is also used to:

- Decrease the melting point of Na_2CO_3.
- Function as an oxidizing agent.

2. Amount of $KNO_3$is specified according to the 1/4 of Na_2CO_3

3. Metalsilicates are not dissolved in acid and acidic mixtures except HF.

$CuSiO_3$+ HF $\rightarrow SiF_4$ (g) (Toxic SiF_4 (g), which must not be inhaled, is produced at constant temperature)

Reactions of metal silicates by Na_2CO_3 fusion,

$$CuSiO_3 + Na_2CO_3 \xrightarrow{\triangle} CuCO_3 + Na_2SiO_3$$

$Al_2(SiO_3)_3$ $\rightarrow$ $Al_2(CO_3)_3$

$ZnSiO_3$ $\rightarrow$ $ZnCO_3$

$CoSiO_3$ $\rightarrow$ $CoCO_3$

$NiSiO_3$ $\rightarrow$ $NiCO_3$

$\downarrow$

Not soluble

$\downarrow$

Water soluble

These carbonates of all cations except sodium and potassium are removed from the solution to be tested for the anion mixtures in order to get rid of their interfering effects.