29. Determination of carbonate in minerals by gravimetric method

Carbonates are important components of many minerals, the most widespread are calcite $CaCO_3$, dolomite (a mixture of $CaCO_3$ and $MgCO_3$, and others. These minerals are raw materials for obtaining lime and cements. Analysis of the content of carbonates in the rock is therefore substantial for many branches of mass production.
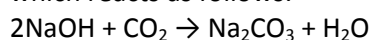
Carbonates are decomposed by diluted acids and gaseous CO_2 is produced. There are two gravimetric methods which apply this reaction: determination of the loss of weight of carbonate due to the escape of carbon dioxide (indirect method), or the CO_2 evolved is absorbed in a suitable medium and the increase in weight of the absorbent is determined (direct method). The direct method is more precise and will therefore be described here.

For decomposition of carbonates we will use dilute HCl, $HClO_4$, or H_3PO_4 acids. The latter seems to be the most convenient because it is not volatile (why?) and its reaction with the mineral can be easily controlled. When using dilute HCl one should insert a short water-cooled condenser between the reaction flask and the absorption train.

We will need two absorbents.

One of these is for water vapor (anhydrous $CaCl_2$ 14-20 mesh, anhydrous $CaSO_4$, or anhydrous $Mg(ClO_4)_2$).$CaCl_2$ is less useful, because it contains sometimes a little free lime which will absorb carbon dioxide, too. This can be avoided by saturating the U-tube containing calcium chloride with dry CO_2 for several hours and then to displace the gas by a current of pure dry air before use. On the other hand, $Mg(ClO_4)_2$ is expensive.

The second absorber is for carbon dioxide. In general use is soda-lime (a mixture of NaOH with $Ca(OH)_{2,aq}$, available also as self-indicating granules, "Carbosorb". They change color when the absorber is exhausted), which reacts as follows:

$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

Water is a product in this reaction, hence it is important to fill 25-35% of the tube with any of desiccants listed above.
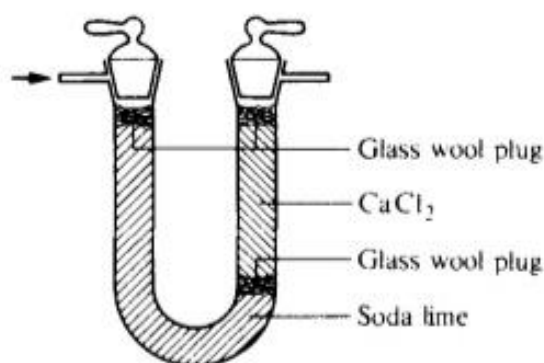

Fig.1. The absorption U-tube as used in this experiment.

The aim of this exercise is to determine the content of carbonates (calculated as calcium carbonate) in a sample of mineral. The sample is decomposed evolving stoichiometric amount of CO_2 which is next absorbed in the U-tube as in the Figure 1. The increase in mass of the U-tube after reaction is attributed to the mass of CO_2 absorbed in it.

Chemicals and equipment:
- H_3PO_4, NaOH in granules, anhydrous $CaCl_2$ prepared in prior of useas described above;
- Four U-tubes, a 100 mL flask, a dropping funnel, small U-tube for NaOH-guard, a bubbler, a stand (see Figure 2 below);
- Mortar with pestle.

Attention! When operating with NaOH use laboratory gloves and protecting glasses – strong bases are very harmful!

Procedure:

1. Fill the dropping funnel (B) and the bubbler (D) with phosphoric(V) acid, the guard U-tube (C) with NaOH. Two U-tubes (E and H) should be filled with $CaCl_2$ (prepared by the laboratory staff in prior to use), and two others (F and G) as shown in Fig. 1. Fit up the apparatus shown in Figure below, but without U-tubes F and G. Ask your teacher for details of connections.
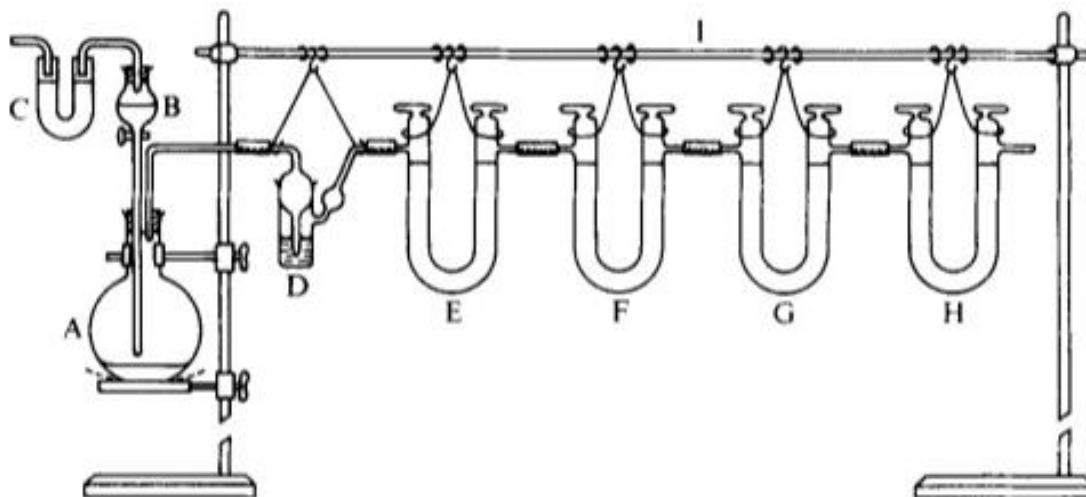

Fig.2. The experimental setup.

2. Make sure the apparatus is gas-tight.
3. Grid a piece of the mineral under analysis to powder. Weigh out accurately 0.4-0.7 g of the sample into the flask A (clean and dry). Wipe the two absorbing U-tubes F and G with a clean linen handkerchief or cloth and leave them in the balance case for ca. 30 min. Open the taps of these U-tubes momentarily to the air and weigh separately. Now fit them in the drying train.
4. Open the taps of the U-tubes.
5. Run in phosphoric acid from the tap funnel into the flask. The acid should cover the solid, 25 mL should be more than suffice. Heat the flask carefully. No more than 2 bubbles of gas per second should pass through the bubbler D.
6. After 25-35 min heat the flask to boiling for 2-3 min. Remove the heater, disconnect the reaction flask A from the bubbler, connect the nitrogen line to the bubbler D (to its open end) and draw dry N_2 through the apparatus at the rate of 2-3 bubbles per second, for 15-20 min.
7. Remove the tubes F and G, close their taps, treat as before and weigh them.
8. From the increase in weigh, calculate the percentage of CO_2 and of corresponding $CaCO_3$ in the sample.

$$M_{CO_2}=44.01 \text{ g/mol}; M_{CaCO_3}=100.09 \text{ g/mol}$$

Report:

The report should contain the masses recorded and the results as percentages as described above.