3. removal of water vapor

$$H_2SO_4 + H_2O \rightarrow H_2SO_4 \cdot H_2O \quad [7]$$

4. removal of traces of H_2SO_4

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2 \quad [8]$$

5. removal of traces of water vapor

$$Mg(ClO_4)_2 + H_2O \rightarrow Mg(ClO_4)_2 \cdot H_2O \quad [9]$$

6. absorption of CO_2

$$2\ NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \quad [10]$$

Start: **Method**

Apparatus

A modified version of the apparatus for digestion, trapping of undesirable gases and CO_2 absorption that was originally described by Allison (1960) is shown in Fig. 15-2. If the same apparatus also is to be used for determination of total organic C, additional traps are needed to remove the N-, S- and halogen-containing gases from the gas stream, as described in Chapter 36 (Sawhney, 1996).

The original apparatus as described by Allison (1960) can be constructed from the following parts (Nelson & Sommers, 1982): ***(A)*** Hoke needle valve to control air flow; (B) 25-cm high soda-lime tower; (C) 100-mL Kjeldahl flask to fit a no. 2 stopper; (D) Allihn four-bulb condenser fitted with a no. 2 stopper at the bottom end and a two-hole no. 2 stopper at the top end; (E) 60-mL open-top

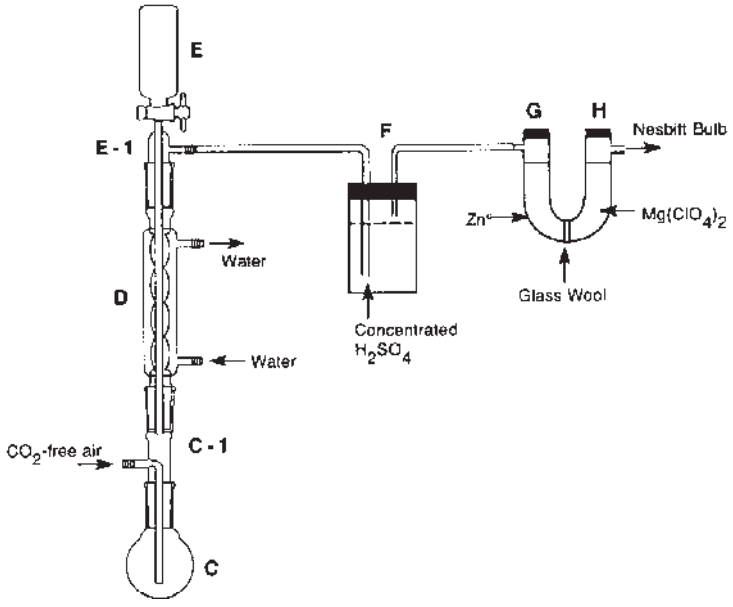

Fig. 1.5-2. Modified Allison apparatus for the gravimetric determination of carbonate (Nelson & Sommers, 1982).

$7H_2O$) in 600 mL of deionized water. Cool the solution, dilute it to approximately 1 L, and store in a well-stoppered container. This solution is approximately 1 M H_2SO_4 and contains 5% $FeSO_4$, to act as an antioxidant.

2. Calcium oxide, Ascarite II or other suitable CO_2 absorbent for the soda-lime tower.
2. Sulfuric acid, concentrated.
3. Granular zinc, 30 mesh $in.^{-1}$.
4. Magnesium perchlorate [$Mg(ClO_4)_2$], anhydrous.
5. Absorbent for carbon dioxide (CO_2): Ascarite II or other suitable absorbent, approximately 8- to 14-mesh $in.^{-1}$ and 14- to 20-mesh $in.^{-1}$; an indicating absorbent is preferred.

Procedure

Transfer a soil sample, previously ground to pass a 30 mesh $in.^{-1}$ sieve, containing not more than 250 mg of $CaCO_3$ equivalent into a 100-mL digestion flask, and connect to the condenser (Fig. 15-2). Weigh the Nesbitt bulb, attach it to the system, and open the valve at the top of the bulb. Pour 25 mL of the digestion acid into the burette at the top of the condenser with the stopcock closed. Allow the acid to enter the digestion flask, and immediately close the stopcock to prevent loss of CO_2. Be sure that the air delivery tube extends at least 5 mm below the acid level in the digestion flask. Turn on the cooling water to the condenser. Adjust the carrier stream to a flow rate of about 2 bubbles s^{-1}, and maintain this rate during digestion. Apply heat slowly, and bring the contents of the flask to a boil in about 4 min. Continue gentle boiling for exactly 3 min more. Remove the flame, adjust the carrier stream to 6 to 8 bubbles s^{-1}, and continue the aeration for 10 min. Shut off the air stream and disconnect the digestion flask from the condenser. Close the stopcock on the Nesbitt bulb, disconnect the Nesbitt bulb from the system, and weigh it immediately. Make a blank determination using the identical procedure but without a sample. Before determining the carbonate content of soil samples, the procedure should be checked with finely ground $CaCO_3$ standards to be sure that a quantitative digestion and determination of carbonate is being obtained.

Calculations

Inorganic carbonate C, mass fraction, $\frac{\text{g C}}{\text{g soil}}$

$$= \left(\frac{\text{g } CO_2 \text{ from sample} - \text{g } CO_2 \text{ from blank}}{\text{g water-free soil}}\right)\left(\frac{\text{atomic weight of C}}{\text{molecular weight of } CO_2}\right)$$

$$= \left(\frac{\text{g } CO_2 \text{ from sample} - \text{g } CO_2 \text{ from blank}}{\text{g water-free soil}}\right) \cdot (0.2727)$$