

## Removal carbonates for CHN

### Digestion of carbonates prior to dry combustion

If organic C is to be determined from combustion techniques (dry or wet), inorganic C must be first removed from calcareous soils. Prior to wet combustion (Walkley-Black), inorganic C is conveniently removed by the addition of dilute sulphuric acid ( $H_2SO_4$ ) and ferrous sulphate ( $FeSO_4$ ). The presence of reduced Fe to minimize oxidation of organic matter.

Inorganic C removal is more difficult before dry combustion. Difficulties include decarboxylation of organic matter, incomplete decomposition of dolomite as well as clays and dissolved organic C losses if the sample is rinsed prior to analysis. To circumvent this last point, Harris *et al.* (2001) proposed a fumigation with concentrated HCl. Removal of carbonates was quantitative. Contrary to what was proposed by the authors, the fumigation should be carried out in glass vessels because both tin and silver capsules will disintegrate when exposed to HCl vapor. Mass changes should be carefully recorded;  $CO_2$  evolution reduces the sample mass while Cl adsorption (formation of green rust) increases it. Finally, the HCl treatment reduces by about 50% the number of samples that can be analyzed before the combustion reactor is exhausted.

For coarse-textured soils, the acid washing procedure of Midwood and Burton (1998) can be used. The procedure is most appropriate for soils with little clays and low carbonate content. A loss of dissolved organic C in the order of 0.1 to 0.5% is common.

### Safety/ Protective equipment



### Equipment/ Reagents

- Falcon Tubes 50mL
- Centrifuge
- Vortex stirrer
- Analytical balance
- Desiccator with drierite
- Oven at 105°C
- HCl 0.5M
- Distilled water

### Soil carbonate decomposition by acid washing (Midwood and Burton, 1998)

1. Grind > 5 g of soils to ~ 20 microns using a mortar and pestle or a ball mill.
2. Dry ground soil overnight at 105°C. Cool in a desiccator and cap the vials.

3. Weigh 1 g of soil into a 50 mL Falcon centrifuge tube. Record the mass of the tube and the mass of the soil to the nearest mg.
4. Add 30 mL of 0.5 M HCl.
5. Stir the suspension on the vortex shaker 3 times over an 8 h period.
6. Leave samples to decant for a further 16 h (total reaction time = 24 h).
7. Taking care not to re-suspend settled materials, transfer the samples to a swinging-bucket centrifuge and centrifuge at 4000 g for 10 min.
8. Decant the supernatant, taking special care not to lose any soil material.
9. Add distilled water to the 30 mL mark.
10. Stir the suspension on the vortex shaker 3 times over an 8 h period and leave the sample to decant for a further 16 h.
11. Centrifuge at 4000 g for 10 min and decant the supernatant.
12. Repeat the washing steps (9-11).
13. Dry the samples at 105°C for a minimum of 24h. Cool in a desiccator.
14. Weigh the tubes + samples to the nearest mg. Calculate the mass change, which represents the amount of carbonates initially present in the sample.
15. Transfer the content of the tubes to a small mortar and pestle and homogenize the sample.
16. Prepare capsules for CHN analysis by dry combustion.
17. Correct dry combustion results for the mass loss (organic C should be expressed as % initial mass).

## References

Harris D, Horwath WR, van Kessel C (2001). Acid fumigation of soils to remove carbonates prior to total organic carbon or carbon-13 isotopic analysis. *Soil Science Society of America Journal* 65: 1853-1856.

Midwood AJ and Boutton TW (1998). Soil carbonate decomposition by acid has little effect on the  $d^{13}C$  or organic matter. *Soil biology and biochemistry* 30: 1301-1307.