

5.5. Organic Matter

*Soil organic matter (SOM) represents the remains of roots, plant material, and soil organisms in various stages of decomposition and synthesis, and is variable in composition. Though occurring in relatively small amounts in soils, **organic matter (OM)** has a major influence on soil aggregation, nutrient reserve and its availability, moisture retention, and biological activity. **Soil Organic Carbon (SOC) ranges from being the dominant constituent of peat or muck soils in colder regions of the world to being virtually absent in some desert soils.** Cultivated, temperate-region soils normally have often than 3 – 4 % SOM, while soils of semi-arid rainfed areas, such as in the WANA region, have normally less than 1.5 % SOM.*

*Most laboratories in the region perform analysis for SOM, which can be measured by either the loss after ignition method, i.e., weight change destruction of organic compounds by H₂O₂ treatment or by **ignition** at high temperature, or by **wet combustion analysis** of soils by chromic acid digestion, which is the standard method for determining total C. Also, organic matter/organic carbon can be estimated by volumetric and colorimetric methods. However, the most common procedure involves reduction of potassium dichromate (K₂Cr₂O₇) by OC compounds and subsequent determination of the unreduced dichromate by oxidation-reduction titration with ferrous ammonium sulfate. This method is referred to as the **Walkley-Black method** (Walkley, 1947; FAO, 1974).*

*While the actual measurement is of oxidizable organic carbon, the data are normally converted to percentage organic matter using a constant factor, assuming that **OM contains 58% organic carbon.** However, as this proportion is not in fact constant, we prefer to report results as **oxidizable organic carbon, or multiplied by 1.33 as organic carbon.***

Apparatus

Magnetic stirrer and Teflon-coated magnetic stirring bar

Glassware and pipettes for dispensing and preparing reagents

Titration apparatus (burette)

Reagents

A. Potassium Dichromate Solution (K₂Cr₂O₇), 1N

- Dry K₂Cr₂O₇ in an oven at 105 °C for 2 hours. Cool in a desiccator (silica gel), and store in a tightly stoppered bottle.
- Dissolve 49.04 g K₂Cr₂O₇ in DI water, and bring to 1-L volume.

B. Sulfuric Acid (H₂SO₄) concentrated (98 %, sp. gr. 1.84)

C. Orthophosphoric Acid (H₃PO₄), concentrated

D. Ferrous Ammonium Sulfate Solution [(NH₄)₂SO₄·FeSO₄·6H₂O], 0.5 M

Dissolve 196 g *ferrous ammonium sulfate* in DI water, and transfer to a 1-L flask, add 5 mL *concentrated H₂SO₄*, mix well, and bring to volume.

E. Diphenylamine Indicator (C₆H₅)₂NH

Dissolve 1 g *diphenylamine* indicator in 100 mL *concentrated H₂SO₄*.

Procedure

1. Weigh 1 g air-dry soil (0.15 mm) into a 500-mL beaker.
2. Add 10 mL **1 N potassium dichromate** solution using a pipette, add 20 mL **concentrated H₂SO₄** using a dispenser, and swirl the beaker to mix the suspension.
3. Allow to stand for 30 minutes.
4. Add about 200 mL **DI water**, then add 10 mL **concentrated H₃PO₄** using a dispenser, and allow the mixture to cool.
5. Add 10 – 15 drops **diphenylamine** indicator, add a Teflon-coated magnetic stirring bar, and place the beaker on a magnetic stirrer.
6. Titrate with **0.5 M ferrous ammonium sulfate** solution, until the color changes from violet-blue to green.
7. Prepare two blanks, containing all reagents but no soil, and treat them in exactly the same way as the soil suspensions.

Calculations

$$M = \frac{10}{V_{blank}}$$

$$\text{Oxidizable Organic Carbon (\%)} = \frac{[V_{blank} - V_{sample}] \times 0.3 \times M}{Wt}$$

$$\text{Total Organic Carbon (\%)} = 1.334 \times \text{Oxidizable Organic Carbon (\%)}$$

$$\text{Organic Matter (\%)} = 1.724 \times \text{Total Organic Carbon (\%)}$$

Where:

M = Molarity of (NH₄)₂SO₄·FeSO₄·6H₂O solution (about 0.5 M)

V_{blank} = Volume of (NH₄)₂SO₄·FeSO₄·6H₂O solution required to titrate the blank (mL)

V_{sample} = Volume of (NH₄)₂SO₄·FeSO₄·6H₂O solution required to titrate the sample (mL)

Wt = Weight of air-dry soil (g)

0.3 = 3 × 10⁻³ × 100, where 3 is the equivalent weight of C.

Technical Remarks

1. **The conversion factor for organic carbon to total organic matter** for surface soils varies from 1.7 to 2.0. In the soils of arid and semi-arid regions; and a value of 1.724 (=1/0.58) is commonly used. The factors 1.334 and 1.724 used to calculate *TOC* and *OM* are approximate, and may vary with soil depth and between soils.
2. **For soils high in OM** (1 % oxidizable OM or more), more than 10 mL potassium dichromate is needed.
3. Soils containing large quantities of chloride (Cl), manganese (Mn) and ferrous (Fe) ions give higher results. The Cl interference can be eliminated by adding silver sulfate (Ag_2SO_4) to the oxidizing reagent. No known procedure is available to compensate for the other interferences.
4. The presence of CaCO_3 up to 50 % of sample weight causes no interferences.
5. **The Walkley-Black method for the determination of SOC** in soils gives about 89% recovery of carbon as compared to the dry combustion method. The conversion factor 0.336 was obtained by dividing 0.003, the milli-equivalent weight of carbon, by 89% and multiplying by 100 to convert to percentage. Chloride interference is eliminated by the addition of the silver sulfate to the digesting acid as indicated. The presence of nitrates and carbonates up to 5 % and 50 %, respectively, do not interfere.
6. **The concentration of H_2SO_4 should be about 6M.** For this reason only 30 mL water are added. (10 mL $\text{K}_2\text{Cr}_2\text{O}_7$ solution plus 20 mL concentrated H_2SO_4 plus 30 mL H_2O give about 6 M H_2SO_4).
7. Air-dried soils seldom contain sufficient amounts of Fe (II) to cause interference. Water-logged soils often contain large quantities of Fe (II), but in most cases this can be oxidized by drying the soil samples prior to analysis.
8. Chloride is oxidized to chromyl chloride, which is volatilized, resulting in high OM values. If high amounts of Cl are present in the sample, add 15 g Ag_2SO_4 to 1-L H_2SO_4 .
9. **Sulfuric acid readily absorbs water.** Therefore, use a fresh reagent.
10. **Elemental C** (e.g., charcoal) is not attacked by dichromate solution in this method.
11. Grinding of the samples is required only to reduce sub-sampling error. It is generally not necessary to pass the ground sample through a sieve (if required use a non-ferrous sieve).