ORGANIC CARBON (WALKLEY-BLACK TITRATION AND COLORIMETRIC METHOD)

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Introduction

Soil carbon is probably the most important component in soils as it affects almost all soil properties.

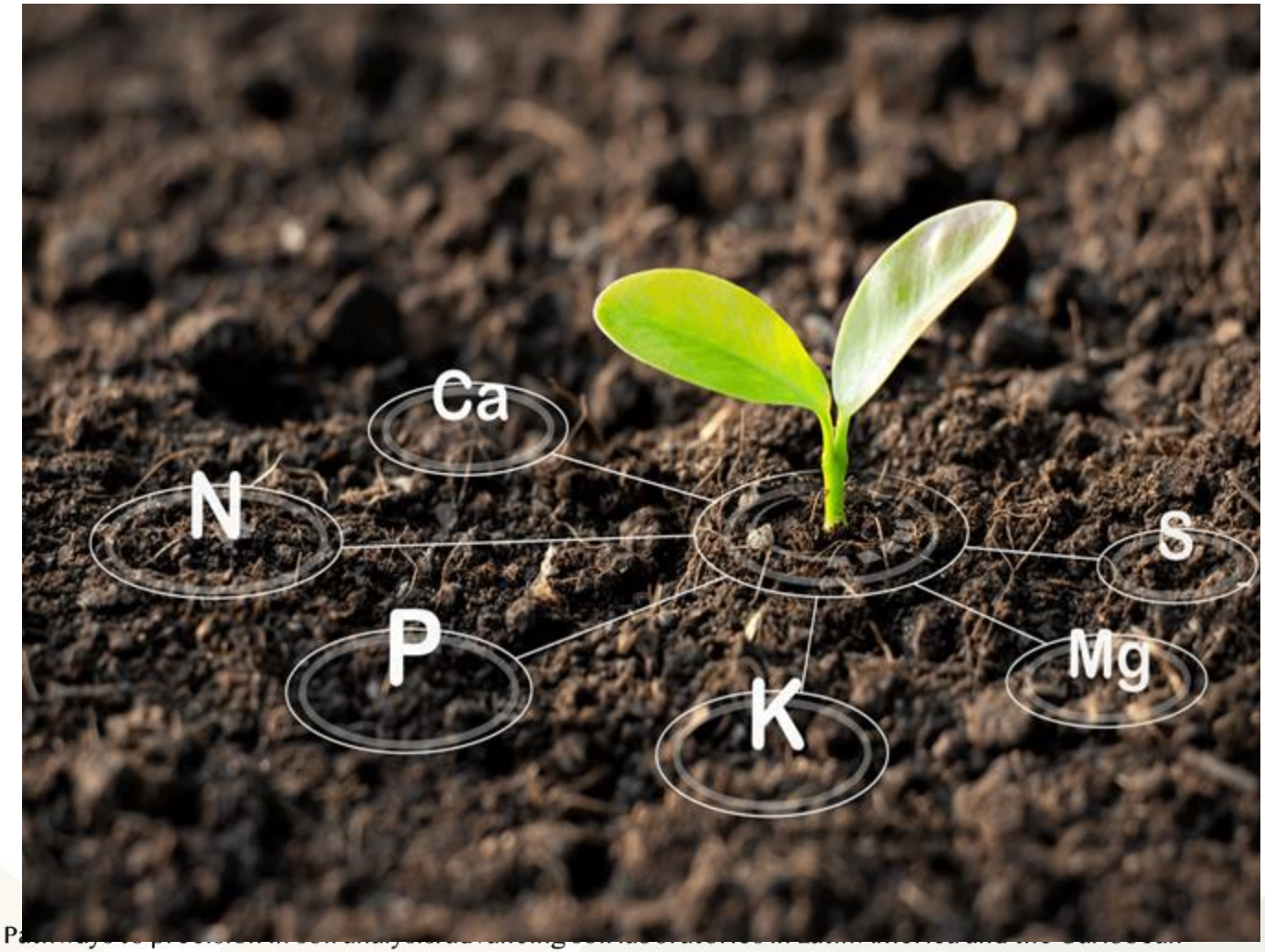
Introduction

PHYSICAL

CHEMICAL

BIOLOGICAL

Introduction



- Better crop yields
- Reduces soil erosion
- Increases biological diversity
- Increases plant nutrient retention

Caminos hacia la Precisión en el Análisis de Suelos: avance de los Laboratorios de Suelos en América Latina y el Caribe

Introduction

Increases in soil organic carbon enhances the biomass and diversity of the soil biodata.

Introduction

The content of organic carbon of mineral horizons can be estimated from the Munsell color of dry and/or moist soil, taking the textural class into account.

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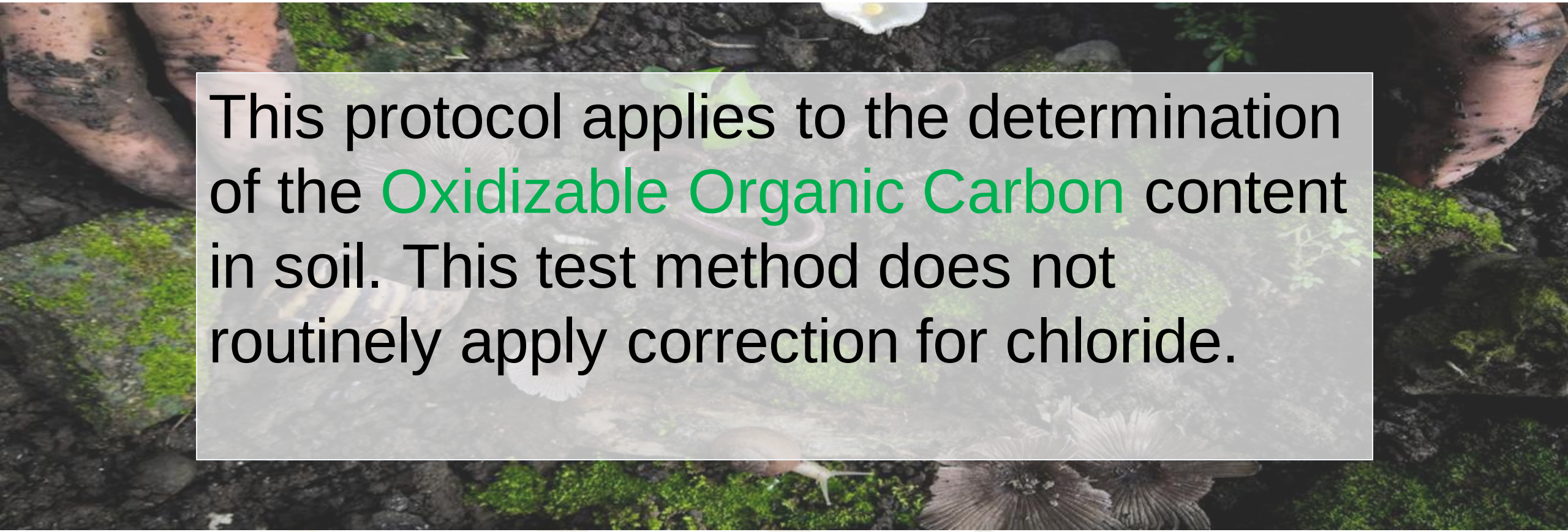
Scope and Field of Application



This protocol applies to the determination of the Oxidizable Organic Carbon content in soil. This test method does not routinely apply correction for chloride.

Principle

POINTS TO BE NOTED:

- Walkley and Black found that on the average about 77% of the organic C was recovered by the heat of dilution procedure, a correction factor of 1.3 be used to account for unrecovered organic C;

- Chloride, ferrous iron and higher oxides of Mn have been shown to undergo oxidation-reduction reactions in chromic acid mixtures leading to incorrect values for organic carbon;

- Smaller sample weights should be used for samples with very high carbon content;

- It is not applicable to soils containing significant amounts of carbonized materials.

Principle in Titration Method

$$6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^+ \longleftrightarrow 2\ Cr^{3+} + 6\ Fe^{3+} + 7\ H_20$$

+

=

The organic C can then be estimated by measuring the remaining unreduced dichromate by back-titrating with ferrous sulphate or ammonium ferrous sulphate using diphenylamine or o-phenanthroline-ferrous complex as an indicator.

Apparatus (Titration Method)

- ❑ **A**nalytical Balance
- ❑ **B**urette, 50 mL
- ❑ **V**olumetric burette/dispenser, 10 mL
- ❑ **V**olumetric dispenser
- ❑ **E**rlenmeyer flasks, 500 mL
- ❑ **M**agnetic stirrer and bar
- ❑ **O**ven (105° C)
- ❑ **V**olumetric flasks, 1000 mL
- ❑ **G**lass rod
- ❑ **B**eaker, 100 mL, 250 mL
- ❑ **F**ume hood
- ❑ **B**urette stand

Materials (Titration Method)

1. Deionized water/distilled water, it should have an EC < 1.5 *10^-3 dS m^-1

2. Potassium dichromate, 0.167 M (10 N)

3. Sulfuric Acid, Concentrated (not less than 96%)

4. Phosphoric Acid, 85% (If Diphenylamine indicator is used)

5. Indicator (either 5.1 or 5.2)
   - 5.1. o-Phenanthroline – Ferrous Complex, 0.025 M
   - 5.2. Barium diphenylamine sulfonate Indicator, 0.16% aqueous solution

6. Titrant (either 6.1 or 6.2)
   - 6.1. Ferrous Sulphate (FeSO4) solution, 0.5 M
   - 6.2 Ferrous Ammonium Sulphate, 0.5 M

Procedure (Titration Method)

1. Weigh 1.0 g of air-dried soil

2. Add 10 mL of 0.167 M $K_2Cr_2O_7^{2-}$

3. Swirl the flask gently to dispense the soil in the solution.

4. Add 20 mL of concentrated sulfuric acid, directing the stream into the suspension

5. Immediately swirl the flask gently until soil and reagents are mixed.

6. Add 200 mL of water to the flask

7. Add 10 mL of 85% H3PO4 (if barium diphenylamine sulfonate indicator is used)

3. Add 3-4 drops of o-phenanthroline or barium diphenylamine indicator.

4. Titrate the solution with 0.5 M FeSO4 solution or 0.5 M $(NH_4)_2Fe(SO_4)_2 * 6H_2O$

5. Observe for color change from blue to red (maroon color in white background)

Calculation (Titration Method)

$$\% \text{ Organic Carbon} = \frac{(V_{blank} - V_{sample}) \times M_{Fe} \times 0.003 \times 100 \times f \times mcf}{W}$$

Where:

V *blank* = volume of titrant in blank, mL

V *sample* = volume of titrant in sample, mL

0.003 = carbon oxidized

f = correction factor, 1.3

W = weight of soil, g

mcf = Moisture correction factor

Principle in Colorimetric Method

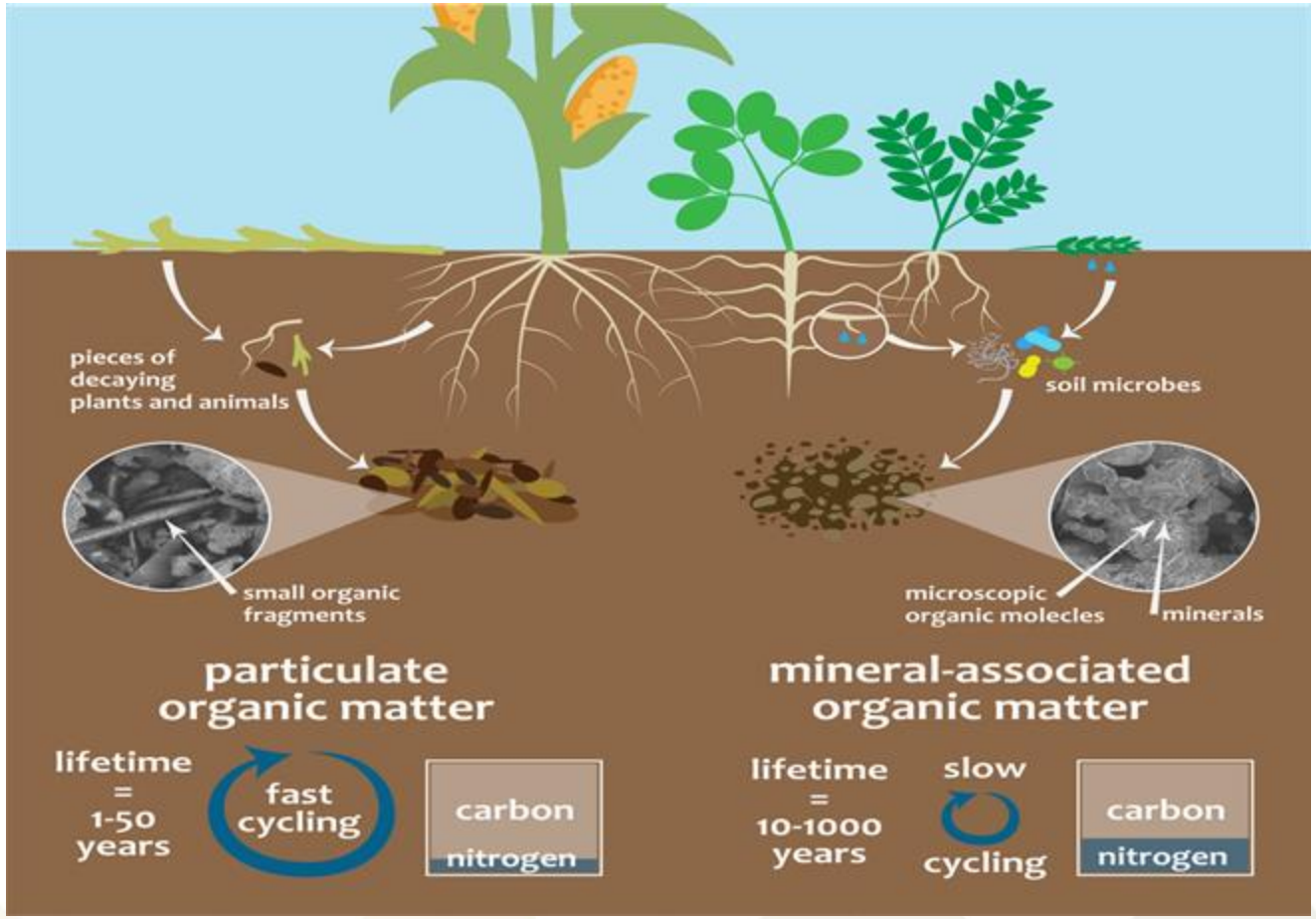
$$2\ Cr_2O_7^{2-} + 3\ C^0 + 16\ H^+ \longleftrightarrow 4\ Cr^{3+} + 3\ CO_2 + 8\ H_2O$$

+

=

Organic carbon can be calculated from the amount of chromic ion formed, using a colorimetric procedure.

Principle (Colorimetric Method)



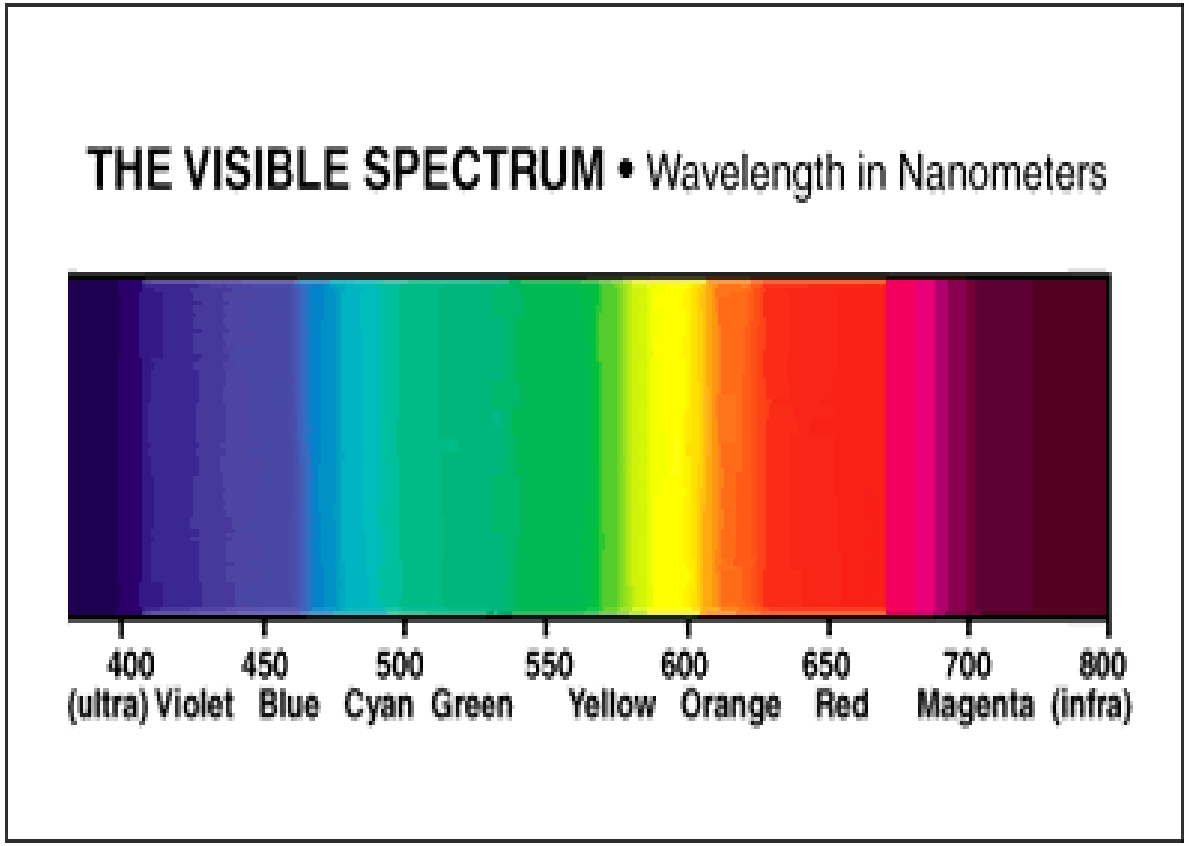
- Walkley & Black chromic acid wet oxidation method.
- OC is oxidized by 0.167 M potassium dichromate solution in concentrated sulfuric acid.

Figure 1. Overview of how particulate and mineral associated organic matter form and function. Retrieved from https://theconversation.com/soil-carbon-is-a-valuable-resource-but-all-soil-carbon-is-not-created-equal-129175

Principle (Colorimetric Method)

- **Green chromic ions (Cr 3+)** produced from the reaction is in direct proportion to the carbon oxidized which is measured by colorimetric estimation.

- Oxidation can be determined by measuring the concentration at wavelength near **600 nm.**



Apparatus (Colorimetric Method)

- ❑ **A**nalytical Balance
- ❑ **S**pectrophotometer
- ❑ **C**entrifuge tubes/glass conical tubes, 50 -70 mL
- ❑ **D**ispensing or volumetric pipettes
- ❑ **G**raduated pipettes
- ❑ **C**alibrated dispenser
- ❑ **G**lass rod
- ❑ **V**olumetric flasks
- ❑ **B**eaker

Equipment and Laboratory Ware

Analytical
Balance

UV-Vis
Spectrophotometer

Conical
Tube

Dispenser

Materials (Colorimetric Method)

1. Deionized water/distilled water, it should have an EC < 1.5 *10^-3 dS m^-1

2. Potassium dichromate, 10% (0.34 M)

3. Sucrose Standard, 4mg/mL

4. Sulfuric Acid, Concentrated (not less than 96%)

Procedure (Colorimetric Method)

PREPARATION OF STANDARDS

1. Place volumes of sucrose standard and DI water in Table 1.
2. Add 2 mL of 10 % Potassium Dichromate and mix.
3. Add 5.0 mL of Sulfuric acid, cool and stand for 30 mins.
4. Add 18 mL DI water. Mix. Stand overnight.
5. Read absorbance set at 600 nm.

PREPARATION OF SAMPLES

1. Weigh soil sample according to Table 2.
2. Add 2 mL of 10% Potassium Dichromate and mix.
3. Add 5.0 mL of Sulfuric acid, cool and stand for 30 mins.
4. Add 20 mL DI water. Mix. Stand overnight.
5. Read absorbance set at 600 nm.

Procedure (Colorimetric Method)

TABLE 1. STANDARD PREPARATION

Mass of OC (mg)	Sucrose Standard (mL)	Deionized Water (mL)
0	0.00	2.00
1	0.25	1.75
2	0.50	1.50
3	0.75	1.25
4	1.00	1.00
5	1.25	0.75
6	1.50	0.50
7	1.75	0.25
8	2.00	0

Procedure

TABLE 2. Recommended weight of sample.

Weight (g)	OC, %	Color
0.1	>2	Black, dark gray,dark brown
0.25	≤0.2	Brown-dark brown, gray-dark gary
0.5	<0.6	brown

Note: Above is just a guide in determining the appropriate weight to be used for each sample based on soil color. % OC may vary per soil color type. Generally, dark colored soils which are described as dark brown to black show a higher content of carbon and nitrogen than those soils which are lighter in color.

Calculation (Colorimetric Method)

$$\% \text{ Organic Carbon} = \frac{\text{mg C (sample)} - \text{mg C (blank)} \times \text{mcf} \times \text{f} \times 100}{\text{W, mg}}$$

Where:

% O.C.	= Organic carbon content of the soil, %
mg C sample	= Analyte/concentration of C in sample
mg C blank	= Analyte/concentration of C in blank
W	= Mass of air-dry sample, mg
mcf	= moisture correction factor
f	= Correction factor, 1.3

Health and Safety

- ✓ Safety glasses, gloves and lab coats must be worn when handling any chemicals
- ✓ Potassium Dichromate: Highly corrosive and is a strong oxidizing agent.
- ✓ Sulfuric Acid: Keep away from naked flames/heat. Always add the acid to the water.

Quality Assurance/Quality Control

ACCURACY TEST

- Participate in **Interlaboratory Proficiency Testing Program** at least once a year.
- Analyze **CRM or QRM.**

Quality Assurance/Quality Control

PRECISION TEST

Perform replicate analysis at most in every 10% samples of a batch. Calculate the % RSD and compare the result with the target precision for the analyte concentration.

Quality Assurance Procedure

CONTROL CHART

Analyzed at least **duplicate of the Check Sample or Internal Reference Material** for every batch of analysis. Plot result in control chart.

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Thank you for listening!!!