A CONTRACTOR OF A CONTRACTOR OF A CONTRACTOR OF A CONTRACTOR OF A CONTRACTOR A CONT	<b>TEST METHODS MANUAL</b> Laboratory Services Division Bureau of Soils and Water Management Department of Agriculture	TN	Л-LSD-04-03
SECTION : SO	IL CHEMISTRY	Issue No.: 2	Effective date: March 22, 2021
SUBJECT : TITRIMETRIC	ORGANIC CARBON (WALKLEY-BLACK - METHOD)	Revision No.: 0	Page 1 of 6

### SCOPE

This method is for the determination of organic carbon in soils. This method is not applicable to soils containing significant amounts of carbonized materials.

### PRINCIPLE

Organic matter in soil may be oxidized by treatment with a hot mixture of  $K_2Cr_2O_7$  and  $H_2SO_4$  according to the following equation:

$$2 \operatorname{Cr}_2 \operatorname{O}_7^{2-} + 3 \operatorname{C}^0 + 16 \operatorname{H}^+ = 4 \operatorname{Cr}^{3+} + 3 \operatorname{CO}_2 + 8 \operatorname{H}_2 \operatorname{O}_2$$

After the reaction, the excess  $Cr_2O_7$  is titrated with FeSO<sub>4</sub>. The  $Cr_2O_7^{2-}$  reduced during the reaction with soil is equivalent to the organic C present in the sample. It must be emphasized that the method assumes that C in soil organic matter has an average valence of zero.

$$6 \operatorname{Fe}^{2+} + 2 \operatorname{Cr}_2 \operatorname{O}_7^{2-} + 14 \operatorname{H}^+ \longrightarrow 2 \operatorname{Cr}^{3+} + 6 \operatorname{Fe}^{3+} + 7 \operatorname{H}_2 \operatorname{O}_7^{3+}$$

### **TEST PRECAUTIONS**

Samples must be air-dried or oven-dried to prevent over estimation of OC/OM, which may occur when significant amount of iron is present. Large inorganic particles (>2 mm) such as gravel, pebbles and rocks present in the sample may also be generally removed with little concern due to their lack of contribution to soil OC/OM and chemical inertness.

Sulfuric acid should be used fresh from the bottle and not left standing in a beaker, as it rapidly picks up moisture from the air. It is satisfactory until the strength falls to <96%. Potassium dichromate, on the other hand, should be prepared fresh every 30 days. During analysis, these reagents must be delivered from a calibrated dispenser to reduce error from manual pipetting and to minimize contact of analyst with chemicals. Sulfuric acid must be added to the sample as quickly as possible since the reaction depends on the heat of dilution of the acid. During mixing of solution, avoid excessive swirling that would result in organic particles adhering to the sides of the flask out of the solution.

### EQUIPMENT

a) Analytical balance

### LABORATORY WARE

- b) Burette, 50 mL
- c) Erlenmeyer flasks, 500 mL
- d) Pipettes

Prepared by:	Reviewed by:	Approved by:	
embgamboa EZRA MAE B. GAMBOA	JP Sancher FLORFINA P. SANCHEZ	GINA PUNILO, Ph.D.	
Document Controller	Head, Soil Chemistry Section	Quality Manager	
THIS IS A CONTROLLED DOCUMENT MAINTAINED ELECTRONICALLY.			
THIS IS UNCONTROLLED WHEN DOWNLOADED, PRINTED AND PHOTOCOPIED.			

## TEST METHODS MANUAL

Laboratory Services Division Bureau of Soils and Water Management Department of Agriculture

# TM-LSD-04-03

Department of Agnealtare		
SECTION : SOIL CHEMISTRY	Issue No.: 2	Effective date: March 22, 2021
SUBJECT : ORGANIC CARBON (WALKLEY-BLACK -	Revision No.: 0	Page 2 of 6
TITRIMETRIC METHOD)		

### CHEMICALS AND REAGENTS

- a) Deionized water/distilled water, it should have an EC <  $1.5*10^{-3}$  dS m<sup>-1</sup>
- b) Potassium dichromate Standard, 0.1667 M: Dissolve 49.04 g of NIST Traceable  $K_2Cr_2O_7$  (dried at 105°C) in deionized water, and dilute the solution to a volume of 1000 mL.
- c) Sulfuric acid, concentrated (not less than 96%): If Cl<sup>-</sup> is present in soil, add Ag<sub>2</sub>SO<sub>4</sub> to the acid at the rate of 15 g per liter.
- d) o-Phenanthroline-ferrous complex, 0.025 M: Dissolve 1.485 g of o-phenanthroline monohydrate and 0.695 g of ferrous sulfate heptahydrate (FeSO<sub>4</sub>.7H<sub>2</sub>O) in water. Dilute the solution to a volume of 100mL. The o-phenanthroline-ferrous complex is also available under the name of Ferroin from the G. Frederick Smith Chemical Co. (Columbus, OH).
- e) Ferrous sulfate (FeSO<sub>4</sub>) solution, 0.5 M: Dissolve 140 g of reagent-grade FeSO<sub>4</sub>.7H<sub>2</sub>O in water, add 15 mL of concentrated sulfuric acid, cool the solution, and dilute it to a volume of 1000 mL with distilled water. Standardize this reagent **daily** by titrating it against 10 mL of 0.1667 M potassium dichromate.

Note: The  $Fe^{2+}$  in this solution oxidizes slowly on exposure to air so it must be standardized against the dichromate daily. Prepare a new solution every 30 days.

Calculation of Molarity of Ferrous Sulfate:

$$M_{Fe2+} = \frac{V_{K2Cr2O7} \times M_{K2Cr2}}{V_{Fe5O4}}$$

<u>6 moles FeSO<sub>4</sub></u> 1 mole K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

=

<u>10 mL x 0.1667 M x 6</u> V<sub>FeSO4</sub>

where  $V_{FeSO4}$  = Volume of FeSO<sub>4</sub> titrant (in mL) in blank

### HEALTH AND SAFETY

Wear proper personal protective equipment (PPE) when conducting the analysis. Use laboratory coat, closed shoes, gas mask or dust mask, and chemical gloves to mitigate the harmful effects of exposure on chemicals.

Chemicals used in the analysis, particularly potassium dichromate and sulfuric acid must be carefully and properly handled to avoid potential skin and/or eye contact, ingestion, or inhalation. Mixing of incompatible materials must also be avoided to reduce the risks of fire and explosion inside the laboratory.

Potassium dichromate is a highly corrosive chemical and a strong oxidizing agent, which emits toxic chromium fumes upon heating. It is a known human carcinogen by the inhalation route of exposure. It is not combustible but enhances combustion of other substances, with risk of fire and explosion on contact with combustible substances. Sulfuric acid, on the other hand, is corrosive to all body tissues and inhalation of vapor may cause

Prepared by:	Reviewed by:	Approved by:
embgamboa	Jp Sanchef	AW
EZRA MÁÉ B. GAMBOA	FLORFINA P. SANCHEZ	GINA P\NILO, Ph.D.
Document Controller	Head, Soil Chemistry Section	Quality Manager
THIS IS A CONTROLLED DOCUMENT MAINTAINED ELECTRONICALLY. THIS IS UNCONTROLLED WHEN DOWNLOADED, PRINTED AND PHOTOCOPIED.		

- Add 10 mL of 0.167 M K<sub>2</sub>Cr<sub>2</sub>O<sub>2</sub> and sylicities the solution.

- For full access, kindly fill out the Document Request
- **Form** on cannot otherwise be clearly discerned.
- Google Form link: and then changes to a dark green. At this point, ad nttps://formstgle/RbCgCdA54prTS60N7harply from blue to red (maroon color in reflected ligh

≤2	brown – dark brown, gray – dark gray
	you! brown

Organic C, % = 
$$(V_{blank} - V_{sample}) (M_{Fe2*}) (0.003) (100) \times CF \times mcf$$
  
where:  $V_{blank}$  = volume of titrant in blank, mL  
 $V_{sample}$  = volume of titrant in sample, mL  
 $M_{Fe2*}$  = concentration of standardized FeSO<sub>4</sub> solution  
0.003 = carbon oxidized  
=  $12 \text{ g C} \times 1 \text{ mole } K_2 Cr_2 O_7 \times 3 \text{ moles } C \times 11 \text{ .}$   
mole 6 moles FeSO<sub>4</sub> 2 moles  $K_2 Cr_2 O_7 \times 1000 \text{ mL}$   
Prepared by:  
 $M_{Fe2*}$  Reviewed by:  
 $M_{Fe2*}$  Approved by: