

Department of Sustainable Natural Resources

SOIL SURVEY STANDARD TEST METHOD

ORGANIC CARBON

ABBREVIATED NAME	OC
TEST NUMBER	C6
TEST METHOD TYPE	A
VERSION NUMBER	2

CAUTION: This procedure involves the use of hazardous chemicals. Refer to laboratory safety guidelines before proceeding.

SCOPE

Estimates of total organic carbon (OC expressed as C) are used to assess the amount of organic matter in soils. The method measures the amount of carbon in plant and animal remains, including soil humus but not charcoal or coal. Levels are commonly highest in surface soils but wide variations from almost zero to above 15% C are possible. Presence of Cl will produce a positive interference in saline soils (>0.5% Cl). The bias resulting from the presence of Cl can be corrected if required.

PRINCIPLE

The determination of soil organic carbon is based on the Walkley-Black chromic acid wet oxidation method. Oxidisable matter in the soil is oxidised by 1 N $K_2Cr_2O_7$ solution. The reaction is assisted by the heat generated when two volumes of H_2SO_4 are mixed with one volume of the dichromate. The remaining dichromate is titrated with ferrous sulphate. The titre is inversely related to the amount of C present in the soil sample.

APPARATUS

- Hot plate with simmerstat control or electric nest as used in macro-nitrogen determinations or bunsen burner with tripod and gauze.
- Heat-resistant sheet on which to cool flasks.
- Fume cupboard.
- 10 mL automatic zero pipette or syringe pipette.

CAUTION: If using an ordinary pipette, use a rubber pipette filler to suck up the potassium dichromate solution which is poisonous.

- 20 mL measuring cylinder or syringe pipette for dispensing concentrated sulphuric acid.
- 250 mL dry erlenmeyer (conical) flasks. 250 mL tall form beakers can be used as an alternative to erlenmeyer flasks for potentiometric titration.
- 200 °C thermometer.
- 50 mL burette or automatic titration unit.
- 1000 mL volumetric flask.
- 100 mL volumetric flask.

REAGENTS

1 N Potassium Dichromate

Dissolve 49.040 g $K_2Cr_2O_7$ AR (dried at 105 °C) in deionised water, transfer to a 1 L volumetric flask and make to volume with deionised water.

Sulphuric Acid 98% w/w

This should be used fresh from the bottle and not left standing in a burette or beaker, as it rapidly picks up moisture from the air. It is satisfactory until the strength falls to <96%.

0.4 N Ferrous Sulphate

Dissolve 112 g $FeSO_4 \cdot 7H_2O$ in 800 mL deionised water containing 15 mL concentrated H_2SO_4 . Dilute to 1 L with deionised water and store in a dark bottle.

"Ferrouin"

Dissolve 1.485 g O-phenanthroline monohydrate and 0.695 g ferrous sulphate in approximately 80 mL deionised water, then dilute to 100 mL. Store in a dark bottle away from light.

PROCEDURE

1. Determine the moisture content of the air-dry soil which has been ground to pass a 0.42 mm sieve. (See [Soil Moisture Content P1A/1.](#)) Weigh accurately enough soil to contain between 10 mg and 20 mg of carbon into a dry tared 250 mL conical flask (between 0.5 g and 1 g for topsoil and 2 g and 4 g for subsoil). (See Note 1.)
2. Accurately add 10 mL 1 N $K_2Cr_2O_7$ and swirl the flask gently to disperse the soil in the solution. Add 20 mL concentrated H_2SO_4 , directing the stream into the suspension. Immediately swirl the flask until the soil and the reagent are mixed. Insert a 200 °C thermometer and heat while swirling the flask and the contents on a hot plate or over a gas burner and gauze until the temperature reaches 135 °C (approximately ½ minute). (See Note 2.)
3. Set aside to cool slowly on an asbestos sheet in a fume cupboard. Two blanks (without soil) must be run in the same way to standardise the $FeSO_4$ solution.
4. When cool (20–30 minutes), dilute to 200 mL with deionised water and proceed with the $FeSO_4$ titration using either the "ferroin" indicator or potentiometrically with an expanding scale pH/mV meter or autotitrator.

"Ferroin" Titration

Add 3 or 4 drops of Ferroin indicator and titrate with 0.4 N $FeSO_4$. As the end point is approached, the solution takes on a greenish colour and then changes to a dark green. At this point, add the ferrous sulphate drop-by-drop until the colour changes sharply from blue-green to reddish-grey. (See Note 3). If the end point is overshoot, add 0.5 or 1.0 mL of 1 N $K_2Cr_2O_7$ and reapproach the end point drop-by-drop. Correct for the extra volume added. If over 8 mL of the 10 mL dichromate have been consumed, the determination must be repeated with a smaller soil sample.

Manual Potentiometric Titration

1. Set an expanded scale pH/mV meter with a platinum electrode and calomel reference electrode to read E(mV). Insert the electrodes and temperature compensator in the solution and stir with a magnetic stirrer. Tall form beakers can be used as an alternative to conical flasks giving more room for the electrodes, temperature compensator and burette.
2. Using one of the unknowns, plot a titration curve by recording values of measured E(mV) and mL titrant (0.4 N $FeSO_4$) added from a burette. The end point is then found on the point of inflexion on the curve (approximately 750 mV). Subsequent titrations are simply discontinued when this point is reached, and the corresponding titrant consumption is then measured. If over 8 mL of the 10 mL has been consumed, the determination must be repeated with a smaller soil sample.

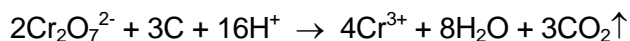
Automatic Potentiometric Titration

Use an autotitrator with a platinum electrode to the mV terminal and calomel reference electrode to the glass electrode terminal. Use a 25 mL autoburette for the 0.4 N $FeSO_4$ titrant. The titration is carried out by first plotting a titration curve as described above and then automatically titrating to the end point (approximately 750 mV) thus determined. Titrator settings are as follows: proportional band 2, delay 5 seconds, direction of titration downscale, burette speed 1.

If over 8 mL of the 10 mL dichromate has been consumed, the determination must be repeated with a smaller soil sample.

CALCULATIONS

From the equation:



1 mL of 1 N Dichromate solution is equivalent to 3 mg of carbon.

Where the quality and normality of the acid/dichromate mixture used are as stated in the method, the percentage carbon is determined from the following:

$$\begin{aligned} \text{Organic Carbon (\%)} &= \frac{0.003 \text{ g} \times N \times 10 \text{ mL} \times (1 - T/S) \times 100}{\text{ODW}} \\ &= \frac{3(1 - T/S)}{W} \end{aligned}$$

Where:

N	=	Normality of $\text{K}_2\text{Cr}_2\text{O}_7$ solution
T	=	Volume of FeSO_4 used in sample titration (mL)
S	=	Volume of FeSO_4 used in blank titration (mL)
ODW	=	Oven-dry sample weight (g)

REFERENCES

Allison, LE in Black, CA et al. 1965, *Methods of Soil Analysis*, pp1372-1378.

Bartlett, GN, Craze, B, Stone, MJ & Crouch, R (ed) 1994, *Guidelines for Analytical Laboratory Safety*. Department of Conservation & Land Management, Sydney.

McLeod, S 1973, Studies on wet oxidation procedures for the determination of organic carbon in soils. CSIRO Division of Soils, *Notes on Soil Techniques*, pp73-79.

NOTES

1. Ferrous iron in soils, if present, leads to high results for the dichromate-ferrous sulphate titration. However, soil samples that have been air-dried for 1 or 2 days contain insignificant amounts of soluble iron compounds, even though ferrous iron had been high in the fresh sample.

Where the chloride content of the soil is high, some interference will occur. This can be suppressed by the addition of silver sulphate to the concentrated sulphuric acid at the rate of 15 g/L. In most cases, chloride affect can be ignored as a chloride content of 1%, for example which is a very high figure, would result in an error of only about 0.1% in the organic carbon content.

Nitrates up to 5% and carbonates up to 50% do not interfere in the determination.

2. It is important that heat be removed when the digesting solution reaches 135° C as the dichromate thermally decomposes at 150 °C causing significant errors.
3. Some soils adsorb "Ferriin" indicator and it might be necessary to filter using a rapid filter paper.
4. Comparative tests of this procedure carried out by CSIRO Division of Soils and NSW Department of Mineral Resources have shown that a correction factor for recovery of carbon is not required.

The effect of charcoal in the soil on organic carbon is unresolved. If charcoal is present, it should be noted or, if desired, removed before testing.