

Chapter 8

Recommended Soil Organic Matter Tests

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The importance of soil organic matter in supplying nutrients, contributing to cation exchange capacity, and improving soil structure, is well recognized. In some states, the organic matter content of the soil is used to adjust N, S, herbicide, and/or lime recommendations. The importance of soil organic matter in herbicide recommendations has rekindled an interest in organic matter analysis. Soil organic matter content is also useful in developing management plans for land application of municipal sewage sludges and other wastes.

Organic matter determinations are usually based on one of two methods:

1. *Weight loss on removal of the organic matter from the mineral fraction by:*
 - a. Oxidation with H_2O_2
 - b. Ignition
 - c. Ignition after decomposition of silicates with HF

2. *Determination of some constituent that is found in a relatively constant percentage of soil organic matter such as:*
 - a. Nitrogen
 - b. Carbon

The weight loss determinations are subject to errors caused by volatilization of substances other than organic materials (H_2O , structural OH, CO_2 from carbonates) and incomplete oxidation of carbonaceous materials. Also, these methods are usually very time-consuming.

Recent interest in weight loss methods has arisen out of a desire to eliminate the use of chromic acid because of the safety and disposal concerns with this reagent. Ball (1964) compared the weight loss of 117 upland, 22 lowland, and 11 organic soils of North Wales at $850^\circ C$ and $375^\circ C$ with organic matter determined by a modification of the Walkley and Black (1934) procedure. Results at both temperatures were highly correlated with organic matter by the Walkley and Black procedure, but the lower temperature was deemed preferable. Goldin (1987) compared the loss of weight on ignition of 60 non-calcareous soils of northwestern Washington and British Columbia with organic carbon determined with a Leco carbon analyzer ($r^2=0.98$). Storer (1984) automated the procedure by developing a computerized weighing system.

Mehlich (1984) extracted "humic matter" with 0.2 M NaOH + 0.0032 M DTPA + 2% ethanol; this method is used in North Carolina. Attempts to use this procedure on Wisconsin soils have resulted in poor reproducibility in replicate samples. It is believed that mobilization of clay may be partly responsible.

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Estimation of organic matter by determination of total nitrogen is not widely used because of the relatively wide variation in nitrogen concentration of organic materials from different sources. However, carbon determinations are used extensively for this estimation, the carbon being determined by:

- a. Dry combustion and measurement of CO₂ evolved (after removal of carbonates)
- b. Chromic acid oxidation and measurement of CO₂ evolved (after carbonate removal)
- c. Chromic acid oxidation to measure easily oxidized material (external heat applied).
- d. Chromic acid oxidation to measure easily oxidized material (spontaneous heating).

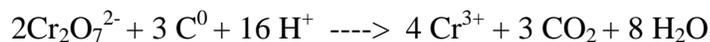
The dry combustion method measures total carbon whereas the chromic acid methods determine only easily oxidizable C. (The carbon in graphite and coal is not oxidized by chromic acid). Combustion methods that directly measure CO₂ evolved require special apparatus and are not well adapted to rapid analysis of a large number of samples unless rather expensive automated and computerized carbon analyzers are used. Consequently, the methods that use chromic acid oxidation to determine easily oxidizable material are often those most commonly used by soil testing laboratories. These methods (c and d) differ primarily in the source and amount of heat used to drive the reaction. Method (c) utilizes an external source of heat which permits heating to a higher temperature than can be achieved with method (d) which derives its heat from the heat of dilution of concentrated H₂SO₄. Consequently, the reaction in method (c) is much faster and oxidation of the organic matter is more complete, but the conditions must be carefully controlled to achieve reproducible results.

A temperature of approximately 120°C is obtained in the heat-of-dilution reaction of concentrated H₂SO₄ (Allison, 1965). This is sufficient to oxidize the active forms of organic C but not the more inert forms. Walkley and Black (1934) recovered 60 to 86% of the organic C in the soils they studied. As a result of this and other work, a recovery factor of 77% is commonly used to convert "easily oxidizable" organic C to total organic C. Later work (Allison, 1960), however, showed that the recovery factor varied from 59 to 94%. The application of external heat, such as is done in the Schollenberger method (Schollenberger, 1927; Schollenberger, 1945), gives a higher recovery of organic C and less variation in percent recovery among different groups of samples. When external heat is applied, temperature control is extremely important. The actual temperature selected is not too critical so long as the procedure is standardized for that temperature. As temperature increases, reaction time required should decrease and precision increase.

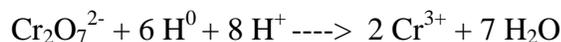
Equations for Dichromate Oxidation of Soil Organic Carbon:

Reaction of $\text{Cr}_2\text{O}_7^{2-}$ with organic matter.

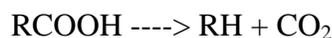
- a. $\text{Cr}_2\text{O}_7^{2-}$ will react with carbon as follows:



- b. Similarly, $\text{Cr}_2\text{O}_7^{2-}$ will react with organic hydrogen as follows:



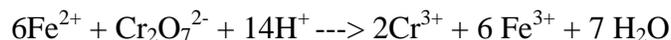
- c. The presence of organic oxygen will decrease the amount of total carbon oxidized by the $\text{Cr}_2\text{O}_7^{2-}$ because of the following reaction:



Reaction (b) tends to compensate for the loss of C due to reaction (c) so that the assumption that each C atom is oxidized from C^0 to C^{4+} reflects the overall electron change in the reaction. The excess $\text{Cr}_2\text{O}_7^{2-}$ is then back titrated with standard Fe^{2+} solution to determine the amount that has reacted, as shown in Equation 2:

Reaction of Fe^{2+} with $\text{Cr}_2\text{O}_7^{2-}$

- a. Ferrous iron reacts with $\text{Cr}_2\text{O}_7^{2-}$ as follows:



Three methods for determining organic matter are given below. The first is the classical Walkley-Black method. The calculation of organic matter assumes that 77% of the organic carbon is oxidized by the method and that soil organic matter contains 58% C. Since both of these factors are averages from a range of values, it would be preferable to omit them and simply report the results as "easily oxidizable organic C." However, these factors are included in the procedures to follow. The second method given below is a rapid method for routine analysis based on colorimetric determination of Cr^{3+} ions produced. The first method is used to standardize the second.

The third method of estimating soil organic matter, loss of weight on ignition, is included because of hazards associated with the use of $\text{Cr}_2\text{O}_7^{2-}$. This ion in a strong acid medium is a powerful oxidant. It is corrosive to skin, mucous membranes, the respiratory tract and the gastrointestinal tract. It may create a cancer risk. Some municipalities restrict the amount of Cr that can be discharged into the sewage system. For these reasons, alternative procedures not involving $\text{Cr}_2\text{O}_7^{2-}$ have been sought.

Errors

Three main sources of error arise with chromic acid digestion: (1) interfering inorganic constituents, (2) differences in digestion conditions and reagent composition, and (3) from the variable composition of the organic matter itself.

Chlorides, if present, reduce $\text{Cr}_2\text{O}_7^{2-}$ and lead to high results. They can be rendered ineffective by precipitation with Ag_2SO_4 added to the digestion acid or by leaching with water prior to digestion. The presence of Fe^{2+} also leads to high results, but drying soils containing Fe^{2+} during preparation of the soil sample for analysis normally oxidizes Fe^{2+} to Fe^{3+} and thus minimizes the amount of Fe^{2+} present. Higher oxides of Mn compete with $\text{Cr}_2\text{O}_7^{2-}$ for oxidation of organic matter, leading to low results. Usually this is not a serious error. Carbonates and elemental C do not introduce any significant error.

Walkley-Black Method
(Walkley and Black, 1934)

Equipment:

1. 500-mL Erlenmeyer flasks.
2. 10-mL pipette.
3. 10- and 20-mL dispensers.
4. 50-mL burette.
5. Analytical balance.
6. Magnetic stirrer.
7. Incandescent lamp.

Reagents:

1. **H₃PO₄, 85%.**
2. **H₂SO₄, concentrated (96%).**
3. **NaF**, solid.
4. **Standard 0.167M K₂Cr₂O₇:** Dissolve 49.04 g of dried (105°C) K₂Cr₂O₇ in water and dilute to 1 L.
5. **0.5M Fe²⁺ solution:** Dissolve 196.1 g of Fe(NH₄)₂(SO₄)•6H₂O in 800 mL of water containing 20 mL of concentrated H₂SO₄ and dilute to 1 L. The Fe²⁺ in this solution oxidizes slowly on exposure to air so it must be standardized against the dichromate daily.
6. **Ferrous indicator:** Slowly dissolve 3.71 g of o-phenanthroline and 1.74 g of FeSO₄•7H₂O in 250 mL of water.

Procedure:

1. Weigh out 0.10 to 2.00 g dried soil (ground to <60 mesh) and transfer to a 500-mL Erlenmeyer flask. The sample should contain 10 to 25 mg of organic C (17 to 43 mg organic matter). For a 1 g soil sample, this would be 1.2 to 4.3% organic matter. Use up to 2.0 g of sample for light colored soils and 0.1 g for organic soils.
2. Add 10 mL of 0.167 M K₂Cr₂O₇ by means of a pipette.
3. Add 20 mL of concentrated H₂SO₄ by means of dispenser and swirl gently to mix. Avoid excessive swirling that would result in organic particles adhering to the sides of the flask out of the solution.

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4. Allow to stand 30 minutes. The flasks should be placed on an insulation pad during this time to avoid rapid heat loss.
5. Dilute the suspension with about 200 mL of water to provide a clearer suspension for viewing the endpoint.
6. Add 10 mL of 85% H₃PO₄, using a suitable dispenser, and 0.2 g of NaF. The H₃PO₄ and NaF are added to complex Fe³⁺ which would interfere with the titration endpoint.
7. Add 10 drops of ferroin indicator. The indicator should be added just prior to titration to avoid deactivation by adsorption onto clay surfaces.
8. Titrate with 0.5 M Fe²⁺ to a burgundy endpoint. The color of the solution at the beginning is yellow-orange to dark green, depending on the amount of unreacted Cr₂O₇²⁻ remaining, which shifts to a turbid gray before the endpoint and then changes sharply to a wine red at the endpoint. Use of a magnetic stirrer with an incandescent light makes the endpoint easier to see in the turbid system (fluorescent lighting gives a different endpoint color). Alternatively use a Pt electrode to determine the endpoint after step 5 above. This will eliminate uncertainty in determining the endpoint by color change. If less than 5 mL of Fe²⁺ solution was required to backtitrate the excess Cr₂O₇²⁻ there was insufficient Cr₂O₇²⁻ present, and the analysis should be repeated either by using a smaller sample size or doubling the amount of K₂Cr₂O₇ and H₂SO₄.
9. Run a reagent blank using the above procedure without soil. The blank is used to standardize the Fe²⁺ solution daily.
10. Calculate %C and % organic matter:

a. **% Easily Oxidizable Organic C**

$$\%C = \frac{(B-S) \times M \text{ of Fe}^{2+} \times 12 \times 100}{\text{g of soil} \times 4000}$$

where:

B = mL of Fe²⁺ solution used to titrate blank

S = mL of Fe²⁺ solution used to titrate sample

12/4000 = milliequivalent weight of C in g.

To convert easily oxidizable organic C to total C, divide by 0.77 (or multiply by 1.30) or other experimentally determined correction factor. To convert total organic C to organic matter use the following equation:

b. **% Organic Matter**

$$\% OM = \frac{\% \text{ total C} \times 1.72}{0.58}$$

Routine Colorimetric Determination of Soil Organic Matter

Equipment:

1. Standard 1 g scoop.
2. Glass marbles with a diameter slightly larger than the mouth of a 50 mL Erlenmeyer flask.
3. 50 mL Erlenmeyer flasks.
4. Digestion oven, capable of temperatures to 90°C, with air circulation fan and fume exhaust.
5. 10 and 25 mL pipettes or dispensers.
6. Standard organic matter samples.

Reagents:

1. **Digestion solution: (0.5 M Na₂Cr₂O₇ • 2H₂O in 5 M H₂SO₄)**: Dissolve 140 g Na₂Cr₂O₇•2H₂O in 600 mL of distilled water. Slowly add 278 mL of concentrated H₂SO₄. Allow to cool and dilute to 1 L with deionized water.

Procedure:

1. Scoop 1 g of soil into a 50 mL Erlenmeyer flask. See Chapter 2 for details on proper scooping techniques.
2. Pipette 10 mL of dichromate-sulfuric acid digestion solution. Include a reagent blank without soil.
3. Cover the Erlenmeyer flasks with glass marbles, which act as reflux condensers, to minimize loss of chromic acid.
4. Place in the digestion oven and heat to 90°C for 90 minutes.
5. Remove samples from the oven, let cool 5 to 10 minutes, remove the glass marble caps, and add 25 mL of water.
6. Mix the suspension thoroughly by blowing air through the suspension via the 25-mL pipettes used to add water or by mechanical shaking.
7. Allow to stand three hours or overnight.

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8. Transfer 10 mL (or other suitable volume of clear supernatant into a colorimeter tube. This can be accomplished conveniently by use of a pipette bank set to dip a suitable distance into the supernatant solutions. Care must be taken not to disturb the sediment on the bottom of the flasks.
9. The blue color intensity of the supernatant is read on a colorimeter at 645 nm with the reagent blank set to give 100% transmittance (or 0 absorbance). The instrument is calibrated to read percent organic matter from a standard curve prepared from soils of known organic matter content.

Alternate Colorimetric Procedure Involving Heat of Dilution

Reagents:

1. **0.5 M Na₂Cr₂O₇•2H₂O**: Dissolve 149 g of Na₂Cr₂O₇•2H₂O in water and dilute to 1 L with deionized water.
2. **H₂SO₄, concentrated, 96%**

Procedure:

1. Scoop 1 g of soil into a 50 mL Erlenmeyer flask. See Chapter 2 for details on soil sample preparation and proper scooping techniques.
2. Add 10 mL of Na₂Cr₂O₇ solution by means of dispenser.
3. Add 10 mL of concentrated sulfuric acid, using a suitable dispenser. A supply of 2% NaHCO₃ should be readily available to neutralize spilled acid on skin, clothing, or lab bench.
4. Allow to react for 30 minutes.
5. Dilute with 15 mL of water and mix.
6. Follow steps 7 through 9 in the colorimetric procedure described on the previous page.

Comment:

A sample exchange involving 25 soil samples among 13 labs in the North Central region showed that results using the routine colorimetric procedure agreed closely with those of the Walkley-Black method. However, the standard deviation was somewhat greater with the routine colorimetric procedure, as might be expected (see Table 8-1). Other modifications of the Walkley-Black method gave greater amounts of variation among labs. This variation would likely have been lower had the comparisons all been made by the same lab. Nevertheless, the results underscore the need to standardize carefully whatever procedure is followed.

Organic Matter Standard Curve for Colorimetric Procedures:

Analyze standard soils of known organic matter content (determined by the Walkley-Black method above or by means of a carbon analyzer) in duplicate by the routine colorimetric method above, except read absorbance on the colorimeter. Then plot the known percent organic matter (or tons organic matter, tons OM/acre) against absorbance readings. Calibrate an instrument scale in % OM (or tons OM/acre) using values obtained from the graph.

Table 8-1. Comparison of organic matter results determined by modifications of the Walkley-Black method.

Comparison	<u>Mean Organic Matter and Standard Deviation</u>					
		Mean	SD		Mean	SD
External heat applied						
Titration (4) vs. Colorimetric (10)	Titration	2.93	0.16	Colorimetric	2.82	0.65
Heat of dilution:						
Titration (4) vs. Colorimetric (4)	Titration	2.93	0.16	Colorimetric	2.58	0.59
Colorimetric procedures:						
Weight (4) vs. Scoop (6)	Weight	2.60	0.53	Scoop	2.97	0.70
Filter (3) vs. Settle (6)		2.15	0.26	Settle	3.21	0.54
Heat of Dilution (6) vs. External Heat (6)	Heat of dil.	2.58	0.59	Ext. heat	2.99	0.68

Results are means of 25 samples ranging from 0.3 to 8.1% organic matter analyzed by 13 North Central region soil testing labs in 1979. Numbers in parentheses indicate number of labs involved in each comparison.

**Alternate Procedure: Loss of Weight on Ignition
(Adapted from Storer, 1984)**

Equipment:

1. Oven capable of being heated to approximately 650°C.
2. Crucibles - 20 mL.
3. Crucible racks, stainless steel, local manufacturer.
4. Balance sensitive to 1 mg in draft-free environment.

Procedure:

1. Scoop 5 to 10 g of dried, ground (10 mesh) soil into tared crucibles.
2. Dry for two hours at 105°C.
4. Record weight to +0.001 g.
5. Heat at 360°C for two hours (after temperature reaches 360°C).
6. Cool to 150°C.
7. Weigh in a draft-free environment to 0.001 g.

Calculation:

Loss of weight on ignition (LOI) is calculated by the following equation:

$$\text{LOI (\%)} = \frac{\text{Weight at 105}^\circ\text{C} - \text{Weight at 360}^\circ\text{C}}{\text{Weight at 105}^\circ\text{C}} \times 100$$

Estimate organic matter:

Estimation of organic matter from LOI is done by regression analysis. Select soils covering the range in organic matter expected in your state or area of testing. Determine percent organic matter by the Walkley-Black method described above. Regress organic matter on LOI. Use the resulting equation to convert LOI to percent organic matter.

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