

**Pathways to precision in
soil analysis: advancing
soil laboratories in Latin
America and the
Caribbean**

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

SOIL ORGANIC CARBON Walkley-Black Method

WORKSHOP
SANTIAGO - CHILLÁN | CHILE
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OBJECTIVE

Reflect on the different critical factors that can influence the results when this method is used to evaluate soil organic carbon.

Soil Organic Matter

SOM refers to all decomposed, partly decomposed and undecomposed organic materials of plant and animal origin

Primary indicator of soil quality

For example, it has influence on

Physical properties

- ✓ Structure and other related properties (Aggregate stability, Porosity, Aeration, Infiltration rate/Surface Runoff, Water storage capacity)
- ✓ Erosion risk
- ✓ Susceptibility to compaction and to superficial crusting
- ✓ Thermal regime, Temperature, Absorption of radiant energy (albedo)
- ✓ Environmental soil conditions (related to temperature, humidity, aeration)

Chemical properties

- ✓ Nutrient reservoir
- ✓ Nutrient availability (N, P, S)
- ✓ CIC
- ✓ Acid-base regulatory capacity

Biological properties

- ✓ Content and activity of soil biota
- ✓ Source of energy and availability of nutrients for microbial processes

Defines the quality and health of a soil

Organic matter quantification

It is quantified	DIRECTLY Weight loss due to calcination	INDIRECTLY Determination of C
Advantages	<ul style="list-style-type: none">• No reagents• Easy implementation	<ul style="list-style-type: none">• Better defined analyte• Acceptable accuracy
Disadvantages	<ul style="list-style-type: none">• Loss of non-organic compound• Low accuracy	<ul style="list-style-type: none">• A factor is required to express the result in OM (1.724)

TOC Analysis

	Dry combustion (Dumas)	Wet Combustion (W&B and others)
Advantages	<ul style="list-style-type: none"> • Good accuracy • Does not generate waste 	<ul style="list-style-type: none"> • Easy implementation • Precision • Few interferences
Disadvantages	<ul style="list-style-type: none"> • Interference in soils with carbonates • Expensive equipment and supplies 	<ul style="list-style-type: none"> • Use of hazardous reagents • Generates waste • Requires the use of a recovery factor to express the result in TOC

Principle of method

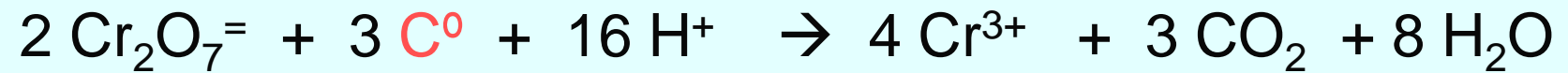
A) OXIDATION: A mass of soil is subjected to the oxidizing action of an acidic solution of potassium dichromate, where the dissolution of sulfuric acid provides the heat necessary for the reaction.

B) TITRATION: the excess dichromate is titrated (reduced) with a ferrous solution, using an appropriate indicator to determine the redox end point.

Critical points of the method

Redox equivalent of organic C

Theoretically, the oxidation of CO by the action of dichromate acting in an acidic medium can be represented in the following redox equation



It is assumed that C is oxidized from the state of C^0 to C^{4+}

$$\begin{aligned} \text{Redox equivalent of OC} &= \text{AW}/4 = 12/4 = 3 \\ \text{meq C} &= 3 \text{ mg} \end{aligned}$$

Critical points of the method

Redox Potential (oxidizing force)

The redox potential of the system depends on:

- The concentration of (sulfuric) acid
- The concentration of the oxidizing agent (dichromate)
- Reaction temperature

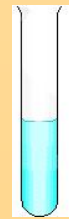
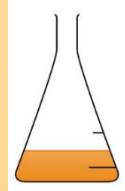
The results may be affected when more than 80% of dichromate is consumed (remember, if you have a very high dichromate consumption, the titration value is very low), then you need to repeat the analysis using less soil.

Critical points of the method

What does the temperature reached in the reaction and its persistence depend on?

Sulfuric/solution ratio: with a 2:1 ratio of sulfuric:dichromate, the maximum temperature is reached (120-140 °C). A quick addition of the sulfuric acid is advisable.

Reaction vessels: The size, architecture and thickness of the glass influence heat dissipation. So it is not the same to use different materials

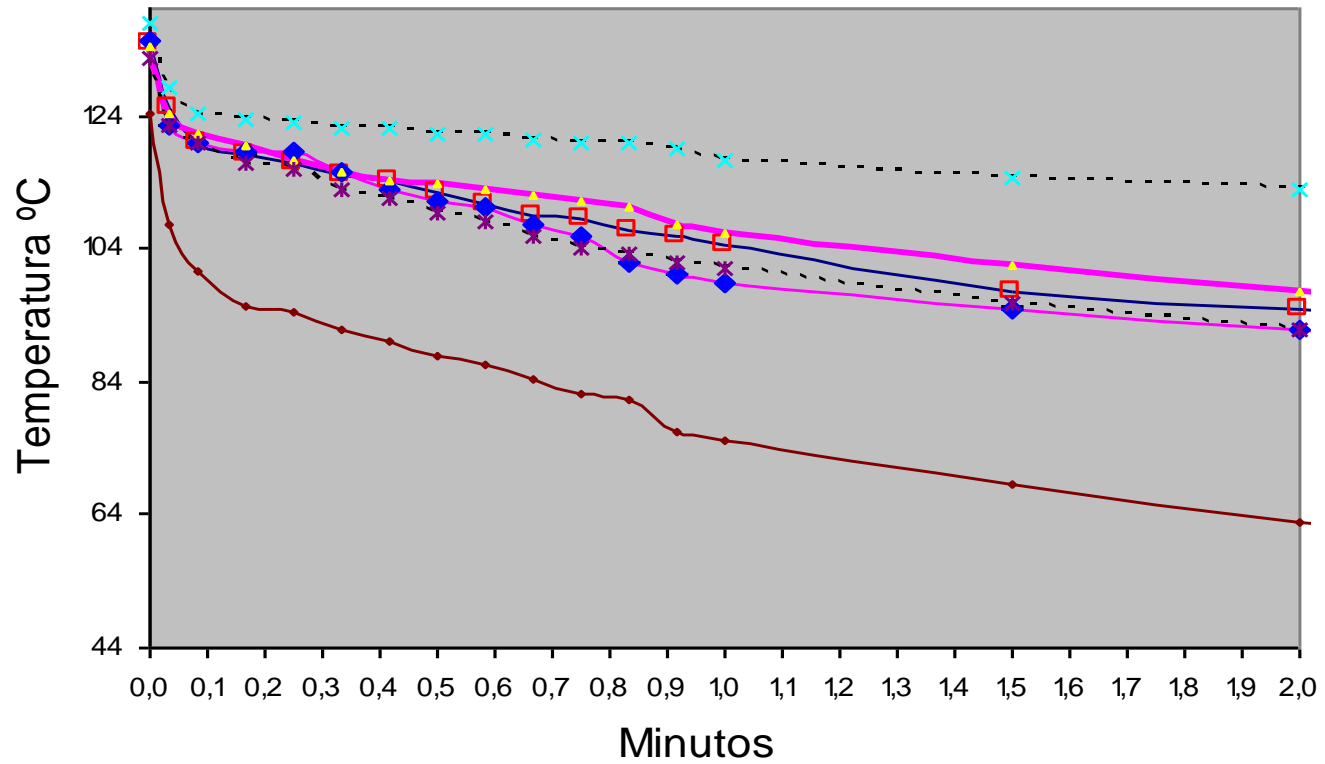


Cup holder and environment: Another heat loss occurs through the cup holder. The design and constituent material affect the permanence of the temperature



Air temperature: Air currents in the reaction zone produce heat loss, so after adding the acid, it is advisable to close the hood and turn it off until the reaction ends and it is necessary to add the water.

Variación de la temperatura de la reacción



Temperature loss varies with the use of different materials and supports



Chemical Interferences

Chlorides: They react with dichromate to give chromyl chloride (CrO_2Cl_2), where 4 Cl is equivalent to 1 C in dichromate consumption $1\% \text{ Cl} = 0.08\% \text{ C}$
It is corrected using a factor, previously washing the soil sample or adding 15 g of silver sulfate to the liter of sulfuric acid.

Iron (ferrous): Normally oxidized to ferric in the soil drying process (Walkley, 1947)

Carbonate contents of up to 50% w/w do not interfere in the determination (Kalra and Maynard, 1991)

Manganese Oxide: Mn oxides present in the soil are poorly reactive (Nelson and Sommers, 1982)

Sample characteristics

- Clay content, allophane material or iron oxides reduce the % of C oxidation (protection of OM in microaggregates)
- Type of organic compounds: degree of humification, OM (No Till) stratification, horizons
- Degree of grinding: several authors recommend a fine grind (0.5 mm) since it improves the homogeneity of the subsample and in some cases improves the % oxidation of C.

REAGENTS

Mohr's salt (ferrous ammonium sulfate): It has the same solubility as ferrous sulfate and reacts in the same way, but it is more stable against oxidation. Likewise, it must be titrated before each test.

Sulfuric Acid: Its concentration should not be less than 96% w/w (36N) since within the range of 90 to 99% there is an almost linear increase in OC recovery of 1% for each % increase in the concentration of the acid. (Walkley,1947)

Potassium dichromate: It is obtained with a sufficient degree of purity to be used as a primary standard once dried in an oven at 110-120 °C for 2 hours. The solutions are very stable and can be preserved indefinitely. Its redox gram equivalent corresponds to one sixth of its molecular weight.

Redox indicators

N-Phenylanthranilic. Mebius (1960) recommends this indicator for having a clear and sharp end point (green to violet).

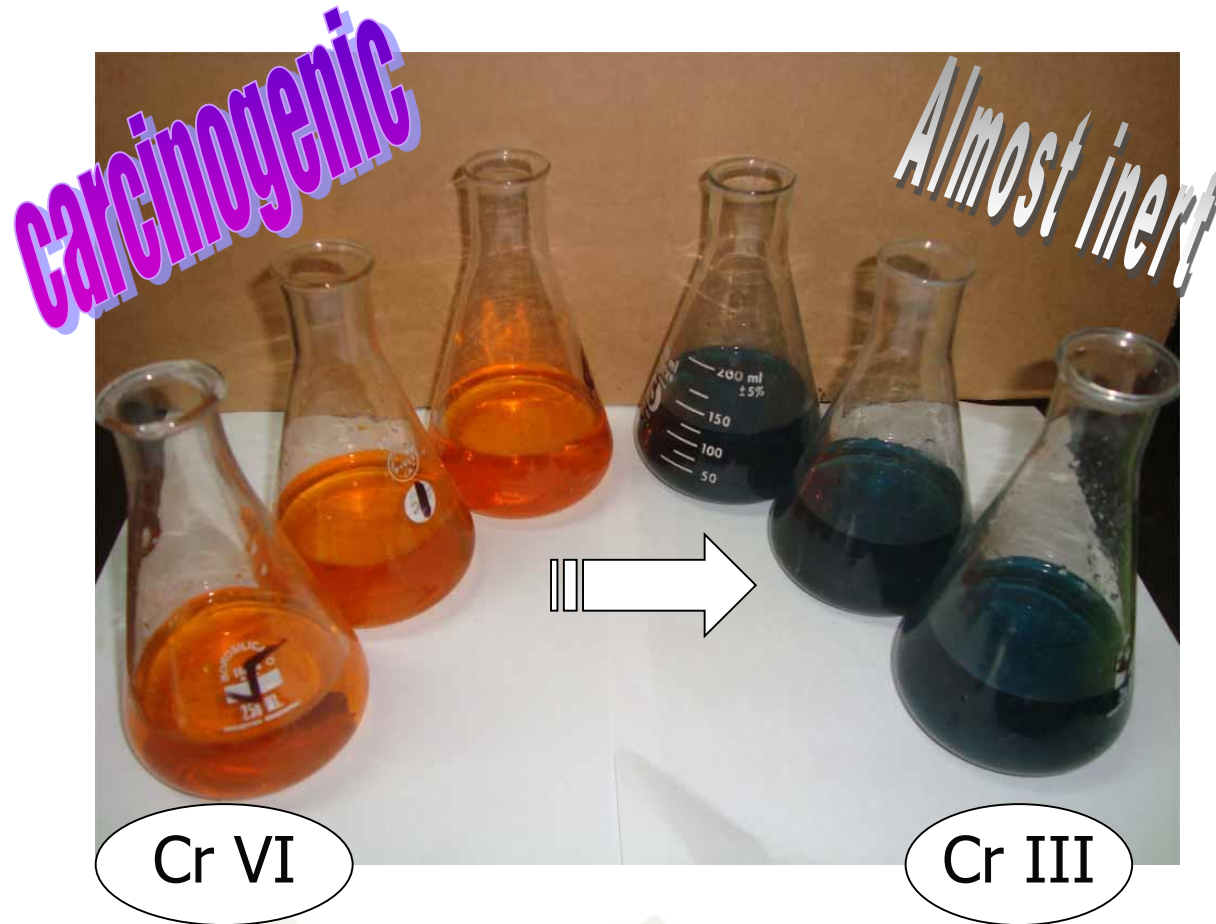
Ba diphenylamine sulfonate. Peech (1947) clarifies that this indicator improves the final point if H_3PO_4 is previously added (blue to green).

Ferrouin (O-phenanthroline + iron sulfate). It is more stable than diphenylamine sulfonates with a sharp endpoint (bright green to red). Not suitable for red soils (oxisols). Does not require the addition of H_3PO_4 as long as the sulfuric concentration is 12 N. It tends to be adsorbed by some soil colloids, so it is recommended to add it just before titration.

Recovery percentage

Referencia	Rango	Promedio	Factor
Bremner&Jenkinson (1960)	57-92	84	1,19
Kalembara (1973)	46-80	77	1,30
Orphanos (1973)	69-79	75	1,33
Richter (1973)	79-87	83	1,20
Nelson&Sommer (1975)	44-88	79	1,27
Bornemisza (1979)	71-77	75	1,33
Galantini (1994)	81-99	90	1,11
Wang (1996)	97-106	99	1,01
Promedio factor			1,21

Waste



It is important to title everything, not just an aliquot



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Standard operating procedure for soil organic carbon

Walkley-Black method
Titration and colorimetric method



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Harmonization

<https://www.fao.org/3/ca7471en/ca7471en.pdf>

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Thank you

