

A BRIEF CRITICAL VIEW OF CHEMICAL OXIDATION METHODS FOR THE DETERMINATION OF TOTAL ORGANIC CARBON IN SOIL

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Abstract: The most used methods in routine analysis to determine total organic carbon in soils (SOC) involve chemical oxidation with $K_2Cr_2O_7$, in a strongly acidic medium. Among them, the Yeomans-Bremner (YB) and Walkley-Black (WB) methods stand out. The disadvantage of these methods is the relatively high amount of Cr(VI) and H_2SO_4 used, which generates a hazardous residue. In addition, they do not fully oxidize organic carbon. Despite being a stronger and more environmentally friendly alternative as an oxidant, $KMnO_4$ is used only for determining labile carbon fractions, probably due to the parallel reactions that occur with permanganate. Methods using an elemental analyzer (EA) are a reliable alternative to chemical oxidation being a reference method for SOC determination. However, the high costs involved in EA methods limit their use in routine analyses. To reduce costs and ensure reliability, chemical oxidation methods are compared with reference methods to obtain factors that allow for correcting results obtained by chemical oxidation methods. This manuscript aims to present the general characteristics of the most used methods for SOC determination, with a critical view of chemical oxidation methods. Finally, a potentially viable alternative for chemical oxidation analysis with reliable results is presented.

Keywords: Organic carbon, Yeomans-Bremner, Walkley-Black, soil, $KMnO_4$, $K_2Cr_2O_7$.

INTRODUCTION

Soil carbon comes mainly from organic matter and carbonate minerals in soils derived from limestone (GATTO et al., 2009). Soil organic matter (SOM) is composed of a mixture of animal and plant residues in different stages of decomposition (MISHRA & SARKAR 2020; IVEZIC et al., 2016). Soil

organic matter plays an essential role in agriculture and the environment due to the promotion and maintenance of soil health, as its level influences several soil properties, such as texture, porosity, cation exchange capacity, nutrient availability, aggregate stability, and microbial activity that are fundamental for ecosystem's sustainability (MISHRA & SARKAR 2020).

Globally, SOM stores more carbon than vegetation and atmosphere combined (LIANG et al., 2019; SCHARLEMANN et al., 2014). Therefore, SOM plays an important role in the global carbon cycling of terrestrial ecosystems, being also a target of interest in studies of carbon transformation and sequestration to understand and predict the global carbon cycle and its role in climate change (LIANG et al., 2019; LEHMANN & KLEBER, 2015).

Total carbon (TC) in soils is the sum of organic (OC) and inorganic (IC) carbon. Most OC is present in the soil organic matter fraction, while IC is widely found in carbonate minerals. Not all soils contain IC, but OC is present in all agricultural soils (NELSON & SOMMERS, 1996a). The total organic carbon content in soils (SOC) correlates with the SOM (BISUTTI et al., 2004; CIAVATTA et al., 1991; YEOMANS & BREMNER, 1988). Therefore, SOC is the main indicator of soil quality and the primary parameter used in carbon cycling studies (LIANG et al., 2019).

Soil organic carbon can be expressed as SOM by multiplying the carbon value by the Van Bemmet factor of 1.724 (100/58) (HEATON et al., 2016; ALLISON, 1965). This factor is based on the assumption that soil organic matter has 58% carbon. However, several studies on using this factor have been reported in the literature, with very variable results, indicating that, at best, it must be used to estimate SOM rather than determining its exact content (HEATON et al., 2016; NAYAK et al., 2019).

The determination of SOC can be performed by dry combustion, wet combustion, and chemical oxidation methods.

ANALYTICAL METHODS FOR SOC DETERMINATION

DRY COMBUSTION METHODS

Dry combustion methods are based on mass loss after ignition (LOI) or the use of an elemental analyzer (EA).

The LOI method consists of the gravimetric determination of organic carbon transformed into CO₂ (reaction 1). The LOI is determined by the volatilized mass of a previously dried soil sample (at 105 °C, for 2 h) after being subjected to high-temperature ignition (350 – 650 °C, for 3 h) (Hoogsteem et al., 2017). ; Escosteguy et al., 2007; Schulte and Hopkins, 1996). The sample mass used in this analysis varies from 4 to 20 g of soil (Hoogsteem et al., 2017; Escosteguy et al., 2007).



The SOC is then calculated from individual conversion factors or through equations developed from the relationship between the LOI and the SOC (NAYAK et al., 2019). However, ambiguous results were produced by some researchers when employing this method (NAYAK et al., 2019).

The dry combustion method involving an EA is considered the most accurate for SOC determination (BISUTTI et al., 2004). It allows fast determinations, requires smaller amounts of sample (2 mg or more), uses certified and high purity analytical reagents, and, therefore, is used as a reference (DO CARMO AND SILVA, 2012; SOON AND ABBOUD, 1991). The analysis involves the thermal oxidation of the OC in an oven and the determination of the released CO₂ (reaction 1). Thermal oxidation at high temperatures (above 1,000 °C) can dispense the use of catalysts. However, at lower temperatures, some catalysts (Cr₂O₃, CuO, CoO, V₂O₅, MnO₂, etc.) are used for

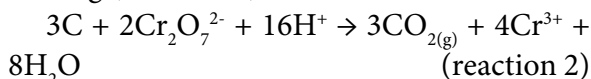
the complete oxidation of OC (NELSON & SOMMERS, 1996a; GREWAL et al., 1991; BISUTTI et al., 2004).

Inorganic carbon interferes in the SOC analysis by dry combustion when it is present in the soil. To produce reliable results, SOC determination must be preceded by treating the soil sample with hydrochloric acid and heating to eliminate IC (carbonate) as CO₂ (NAYAK et al., 2019; BISUTTI et al., 2004).

Despite the relatively high reliability provided by analyses involving the use of an EA, the high cost of acquiring and maintaining the equipment limits the wide application of this method, making the use of alternative methods more attractive, especially in field research.

WET COMBUSTION METHODS

Wet combustion involves the determination of SOC after previous IC removal by measuring the CO₂ produced in the chemical oxidation of OC by K₂Cr₂O₇ in an acidic medium and heating (reaction 2).



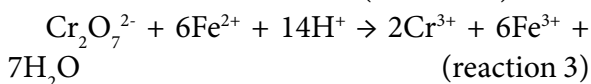
The generated CO₂ can be determined by infrared spectrometry (APHA-AWWA, 1995; THOMAS et al., 1990), thermal conductivity (GÁCS & PAYER, 1989), turbidimetry (PANIZ et al., 2001), gravimetry (ALLISON et al., 1986), ion chromatography (FUNG et al., 1996) or acid/base titration (NELSON & SOMMERS, 1986b). Generally, it is a fast, accurate, and suitable method for samples with high chloride content and rich in organic matter (BISUTTI et al., 2004).

CHEMICAL OXIDATION METHODS

Chemical oxidation methods are widely used in SOC determination (GATTO et al., 2009). Similar to wet combustion methods, these methods perform the oxidation of OC with K₂Cr₂O₇ in an acidic medium with

heating (reaction 2) but measure the excess oxidant instead of the CO₂ produced.

The chemical oxidation methods most used in research and analysis in routine laboratories are undoubtedly the Walkley-Black (WB) and Yeomans-Bremner (YB) methods because they are simple, fast, and inexpensive (NAYAK et al., 2019; PEREIRA et al., 2006; GATTO et al., 2009; BISUTTI et al., 2004; YEOMANS & BREMNER, 1988; WALKLEY & BLACK, 1934). In both methods, the OC is oxidized with a mixture of K₂Cr₂O₇ and concentrated H₂SO₄, and the excess oxidant is titrated with ammoniacal ferrous sulfate (reaction 3).



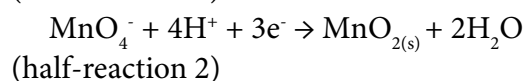
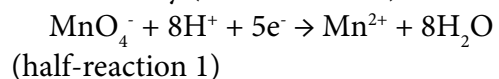
Basically, the main difference between these methods is the external heating source used in OC oxidation. In the WB method, heating occurs only by the heat produced in the mixture of acid and water, although the literature reports variations of this method that employ external sources to raise temperatures above 135 °C (NAYAK et al., 2019; BISUTTI et al., 2004; PEREIRA et al., 2006; DELL'ABATE et al., 1998; CIAVATTA et al., 1991). In the YB method, heating is performed by an external source, leaving the OC to oxidize at 170 °C for 30 minutes (GATTO et al., 2009; PEREIRA et al., 2006; YEOMANS & BREMNER, 1988).

In the WB method, correction factors must be applied since complete oxidation of the OC in the sample does not occur (NAYAK et al., 2019; GATTO et al., 2009; WALKLEY & BLACK, 1934). On the other hand, according to Yeomans and Bremner, heating the mixture at 170 °C for 30 min would be sufficient for the complete oxidation of OC (GATTO et al., 2009; YEOMANS & BREMNER, 1988). However, later studies demonstrated the need to apply correction factors because the YB method also did not promote the complete oxidation of OC in the evaluated samples (GATTO et al., 2009; PEREIRA et al., 2006).

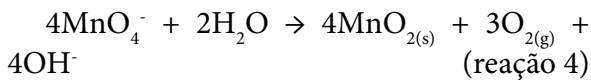
The main drawback of methods based on chemical oxidation is the large amount of K₂Cr₂O₇ and concentrated H₂SO₄ used, which generate hazardous waste to the environment (WANG & WANG, 2022; SATO et al., 2014; MYLAVARAPU, 2014). Chromium is highly carcinogenic and mutagenic and has a high reproductive, dermal, and inhalation toxicity potential (ABNT, 2009). The oxidation of organic matter with K₂Cr₂O₇ and concentrated H₂SO₄ subjected to heating exposes the analyst to several risks. In addition, the commercialization of H₂SO₄ is controlled by security agencies in several countries, which makes its acquisition difficult. For these reasons, some laboratories opted to discontinue these methods, such as the National Severe Storms Laboratory (NSSL) and launched the search for alternative methods for determining TOC (LAL et al., 2000).

KMNO₄ AS AN ALTERNATIVE CHEMICAL OXIDANT

Potassium permanganate (KMnO₄) is a stronger oxidant that produces a more environmentally friendly waste than K₂Cr₂O₇ (WANG & WANG, 2022). However, it has not been used for SOC determination due to the different reaction products that can occur depending on changes in the reaction medium (SKOOG *et al.*, 2006). At pH < 1.0, MnO₄⁻ is reduced to Mn²⁺, a soluble and colorless cation (half-reaction 1). At pH > 1.0, MnO₄⁻ is reduced to MnO₂, a black oxide of low solubility (half-reaction 2).



Moreover, aqueous solutions of KMnO₄ are not completely stable because this oxidant decomposes with water (Burgot, 2012) (reaction 4).



Literature reports an extensive use of KMnO_4 to determine only a fraction of OC, the permanganate oxidizable carbon or labile carbon (CULMAN et al., 2021; SI et al., 2021; SINGH et al., 2018, DE SOUZA et al., 2016, WANG et al., 2015, FRAGA et al., 2015, VERMA et al., 2013, MANDAL et al., 2011, KALISZ et al., 2012, CHAN et al., 2001; BLAIR et al., 1995). This parameter aims to quantify the biologically active carbon in the soil and is used to assess the impacts on soil quality due to alternative management practices (FRAGA et al., 2015). However, there are no complete studies reporting its use in SOC determination, which suggests that any attempt has not been successful yet.

The concentration of KMnO_4 used in the labile carbon determination is generally relatively low and may be insufficient for the oxidation of organic carbon in soils. A high amount of this oxidant causes the formation of MnO_2 , even under conditions of high acidity, making its use as an oxidizing agent in OC determination unfeasible.

In some recently preliminary studies (DE SOUSA et al., 2019; AZEVEDO et al., 2017; AZEVEDO et al., 2016), the oxidation of potassium biphthalate, an important standard of organic matter used in investigations for the determination of total organic carbon (KIM et al., 2018), has been successfully performed using KMnO_4 as a chemical oxidant. In these studies, we sought to find more favorable reaction conditions (time, temperature, and acidity) for organic matter oxidation. The results of these studies demonstrated that KMnO_4 is a suitable alternative to replace $\text{K}_2\text{Cr}_2\text{O}_7$ in the determination of SOC by chemical oxidation, which would be advantageous since it produces less hazardous waste.

It is worth mentioning that $\text{K}_2\text{Cr}_2\text{O}_7$ is

widely used in routine analyses to determine SOC despite this oxidant not being capable of completely oxidizing the organic carbon. Hence, total OC determination requires correction factors to adjust the SOC value obtained by methods with $\text{K}_2\text{Cr}_2\text{O}_7$. Correction factors are determined by comparing chemical oxidation and dry combustion methods with EA. Therefore, in case KMnO_4 is not able to promote the complete oxidation of soil organic carbon, it does not represent a potential problem, given that these corrections are widely adopted on the chemical oxidation methods already consolidated.

CONCLUSION

Dry combustion methods involving the use of an elemental analyzer are the most reliable for SOC determination. However, the high cost of the analysis motivates the search for alternative methods. The most used ones involve chemical oxidation and use a toxic reagent, $\text{K}_2\text{Cr}_2\text{O}_7$, which does not completely oxidize organic carbon, making them dependent on correction factors determined by elemental analyzers. Hence, they are not completely decoupled from dry combustion methods. Potassium permanganate is a potential substitute for $\text{K}_2\text{Cr}_2\text{O}_7$. Although KMnO_4 probably will not fully oxidize the organic matter, similarly to $\text{K}_2\text{Cr}_2\text{O}_7$, it has the added benefit of being a more environmentally friendly reagent with a lower hazardous potential.

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