Artigo

A GREEN AND RELIABLE TITRIMETRIC METHOD FOR TOTAL ORGANIC CARBON DETERMINATION WITH POTASSIUM PERMANGANATE

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The determination of total organic carbon in soils, fertilizers, sewage sludge, sediments, and humic extracts is widely performed by chemical oxidation methods with $K_2Cr_2O_7$. The Yeomans-Bremner (YB) method is currently the one that stands out the most. The drawback of these methods is the large amount of concentrated H_2SO_4 used, which generates a large amount of hazardous waste. This work proposes using $KMnO_4$ as an alternative to $K_2Cr_2O_7$ for a lower consumption of H_2SO_4. The method uses the back titration of Fe^{2+} added to consume both the MnO_2 produced and the excess $KMnO_4$ that was not consumed in the OM oxidation. A non-trivial and yet not explored stoichiometry was applied for this purpose, providing a success not yet achieved in using permanganate to determine TOC by titration. The ideal condition for the oxidation of OC was determined by the analysis of a potassium hydrogen phthalate standard and involved the use of 0.125 mol L^{-1} H_2SO_4 and temperature of 70 °C, obtaining a significant advantage over the YB method (concentrated H_2SO_4 and 170 °C). The proposed method was applied to the analysis of soil samples, producing conversion factors for soil organic carbon that varied between 0.652 and 1.12.

Keywords: Yeomans-Bremner; soil analysis; permanganate; organic carbon; hydrogen phthalate.

INTRODUCTION

Soil organic matter (SOM) is a mixture of animal and plant residues in different stages of decomposition.[1-3] It plays an important role in agriculture and the environment due to the promotion and maintenance of soil health and global carbon storage.[1-8] The total organic carbon (TOC) content, or organic carbon (OC), allows the estimation of the amount of organic matter (OM) in soils, fertilizers, sewage sludge, sediments, and humic extracts.[9-13] Therefore, TOC is one of the main indicators of soil quality,[8] being a parameter used in studies of carbon cycling and soil quality assessments.[4,14] The analytical methods for determining TOC include dry combustion, wet combustion, and chemical oxidation.[15]

Dry combustion methods involving an elemental analyzer (EA) are considered the most accurate for determining TOC, making them a reference for other methods.[10] Dry combustion methods involve the thermal oxidation of OC in an oven and the determination of the released CO_2.[10,16,17] The results produced are reliable when the treatment of the sample to eliminate inorganic carbon (IC) precedes the analysis, which interferes with the results obtained.[10,16,18] However, the high costs of acquiring and maintaining an EA limit the application of the dry combustion methods. Thus, especially in field research, using an alternative method is more convenient, mainly because it can be performed in any soil analysis laboratory despite the need for equipment availability.

Wet combustion involves the determination of TOC by measuring the CO_2 produced in the oxidation of OC by $K_2Cr_2O_7$ in acidic conditions and heating after the previous removal of IC. CO_2 can be determined by infrared spectrometry,[19,20] thermal conductivity,[21] turbidimetry,[22] gravimetry,[23] ion chromatography[24] or acid/base titration.[25] In general, these methods are fast, accurate, and suitable for samples with high chloride content and rich in OM.[10]

Methods involving chemical oxidation are the most used in determining TOC.[15,26,27] As with wet combustion methods, they are based on the oxidation of OC with $K_2Cr_2O_7$ in an acidic medium and heating but involve measuring the excess oxidant rather than the CO_2 produced. The 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.[10,13,18,26,28,29] In both methods, the OC is oxidized with a mixture of $K_2Cr_2O_7$ and concentrated H_2SO_4, and the excess oxidant is titrated with ferrous ammonium sulfate. Essentially, the main point of divergence between the WB and YB methods is the external heating source employed in the OC oxidation reaction. In the WB method, heating occurs only by the heat produced in the mixture of acid and water, although the literature reports variations in the method application that uses external heating sources to achieve temperatures above 135 °C.[12,28,30] In the YB method, heating is performed by an external source, leaving the OC to oxidize at 170 °C for 30 minutes.[13,26,28]

Correction factors are applied in chemical oxidation methods as they do not promote the complete oxidation of OC.[15,18,26,28,29] The correction factors can assume a wide range of variations depending on the analyzed soil. Pereira *et al.*[28] performed the determination of TOC in different types of soils using chemical oxidation methods (YB, modified YB, modified WB, and a method employed by EMBRAPA)[31] and dry combustion (muffle furnace and EA). Taking the EA method as a reference, the correction factors ranged from 0.37 to 2.62. For the YB method, this variation was from 0.64 to 2.28.

The main drawback of chemical oxidation methods is the large amount of concentrated H_2SO_4 used, which generates hazardous waste.[32-34] Oxidation of OM with $K_2Cr_2O_7$, concentrated H_2SO_4, and heating exposes the analyst to several risks. In addition, H_2SO_4 purchase is controlled by security agencies in several countries, which makes its acquisition difficult.[35-38] For these reasons, some laboratories, such as the National Severe Storms Laboratory

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(NSSL), opted to discontinue the use of these methods and dedicated themselves to the search for alternative methods for the determination of TOC.[39]

Potassium permanganate ($KMnO_4$) is a stronger oxidant than $K_2Cr_2O_7$.[40] The literature reports extensive use of $KMnO_4$ for the determination of only a fraction of OC, called permanganate oxidizable carbon or labile carbon.[41-53] Labile carbon quantifies the biologically active carbon in the soil and is used to assess the impacts of alternative management practices on soil quality.[46,51,52] However, up to date, there are no reports involving its use in the TOC determination, which suggests that any attempt to determine this parameter has not been successful.

This work proposes the use of $KMnO_4$ as an alternative oxidizing agent to $K_2Cr_2O_7$ for titrimetric determination of TOC to generate a more environmentally friendly waste with the advantage of reducing acid consumption. For this, the ideal reaction conditions (time, temperature, and acidity) for the oxidation with $KMnO_4$ were evaluated and identified through the oxidation undergone by potassium hydrogen phthalate (KHP). Potassium hydrogen phthalate is an important OM standard used to determine TOC.[54-56] The TOC of soil samples was determined by the proposed method and compared with the reference method of Yeomans and Bremner (YB).

EXPERIMENTAL

Reagents and materials

The following reagents were used in its analytical grade: $C_8H_5O_4K$ (KHP, 99.95%, Vetec, Duque de Caxias, Brazil), $Na_2C_2O_4$ (99%, Vetec, Duque de Caxias, Brazil), $K_2Cr_2O_7$ (99.9%, Merck, Duque de Caxias, Brazil), $KMnO_4$ (99%, Proquimios, Rio de Janeiro, Brazil), *o*-phenanthroline (Proquimios, Rio de Janeiro, Brazil), H_3PO_4 (85%, Sigma-Aldrich, Duque de Caxias, Brazil), H_2SO_4 (95-98%, Proquimios, Rio de Janeiro, Brazil), $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (98.5-101%, Isofar, Duque de Caxias, Brazil) e $FeSO_4 \cdot 7H_2O$ (99%, Sigma-Aldrich, Duque de Caxias, Brazil). The $C_8H_5O_4K$ was ground in a mortar and dried at 105 °C. All other reagents were used as they were commercially obtained. Solutions were prepared in distilled water. Soil samples were donated by the Soil Laboratory of the Agronomy Institute of the Universidade Federal Rural do Rio de Janeiro and are classified in the Brazilian Soil Classification System[57] as: *latossolo* (profile 88, horizon A, coordinates 7508038/602084 UTM, WGS84), *chernossolo* (profile 202, horizon A, coordinates 7506551/602447 UTM, WGS84), *gleissolo* (profile 59, horizon A, coordinates 7509474/604061 UTM, WGS84) and *cambissolo* (profile 74, horizon A, coordinates 7504384/603060 UTM, WGS84) equivalent to oxisols, molisols, entisols (Aqu-alf-and-ent-ept-) and inceptisols, respectively, in the Soil Taxonomy classification.[58]

The OC oxidation procedures were carried out in a Quimis® dry block digester (model Q327-A242, Diadema, Brazil), preheated to the working temperature. Class A volumetric flasks and pipettes were used.

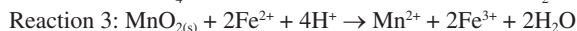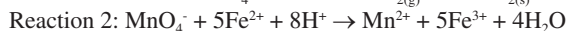### Preparation and standardization of standard solutions

The 0.1666 mol L^{-1} $K_2Cr_2O_7$ e 0.07015 mol L^{-1} $Na_2C_2O_4$ standard solutions were prepared by dissolving 49 g (± 0.0001 g) of $K_2Cr_2O_7$ and 9.4 g (± 0.0001 g) of $Na_2C_2O_4$, respectively, in water with posterior dilution (1000.0 mL) in a volumetric flask.

The 0.2 mol L^{-1} $KMnO_4$ solution was prepared by dissolving 63.2 g de $KMnO_4$ in 2000 mL water. This solution was heated at 100 °C for 30 minutes, filtered through glass wool, stored in an amber bottle, protected from light, and kept at room temperature. This solution was standardized by titrating 50.00 mL of a 0.07015 mol L^{-1} $Na_2C_2O_4$ solution with 40 mL of 3.0 mol L^{-1} H_2SO_4 solution. The 0.02 mol L^{-1} $KMnO_4$ solution was prepared by diluting the 0.2 mol L^{-1} $KMnO_4$ solution and, later, standardizing it with 25.00 mL of 0.07015 mol L^{-1} $Na_2C_2O_4$ standard solution mixed with 20 mL of 3.0 mol L^{-1} H_2SO_4 solution.

The 0.2 mol L^{-1} ferrous ammonium sulfate solution was produced by dissolving 156.8 g of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ in 100 mL of concentrated H_2SO_4 and then diluting it in water until completing 2000.0 mL. Then, 10.00 mL of this solution was mixed with 20 mL of 3.0 mol L^{-1} H_2SO_4 solution and subsequently titrated against 0.02 mol L^{-1} $KMnO_4$ solution. Standardizations were performed in duplicate.

Proposed method

The proposed method basically consisted of oxidizing the OC with 0.2 mol L^{-1} $KMnO_4$ (Reaction 1) and posteriorly reacting the excess of $KMnO_4$ (Reaction 2) and the MnO_2 produced (Reaction 3) with 0.2 mol L^{-1} Fe^{2+}. Finally, the excess Fe^{2+} was titrated with 0.02 mol L^{-1} $KMnO_4$ (Reaction 2).

Reaction 1: $3C + 4MnO_4^- + 4H^+ \rightarrow 3CO_{2(g)} + 4MnO_{2(s)} + 2H_2O$
Reaction 2: $MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$
Reaction 3: $MnO_{2(s)} + 2Fe^{2+} + 4H^+ \rightarrow Mn^{2+} + 2Fe^{3+} + 2H_2O$

For the development and evaluation of this method, the percentage of oxidized carbon (%OC) was determined in a high purity KHP standard, under different conditions of acidity, temperature, and reaction time, as listed in Table 1. The influence of the KHP mass was also investigated (Table 1). The conditions that provided the best %OC in the KHP samples, closer to 100%, were used to analyze soil samples (Table 1).

The analysis comprised of weighing the sample, with an accuracy of ± 0.1 mg, in a 100 mL digestion tube, to which 10.00 mL of 0.2 mol L^{-1} $KMnO_4$ solution and 10 mL of H_2SO_4 were added. The digestion tube was inserted into the digester block and kept under

Table 1. Reaction conditions used in the study of the oxidation of organic matter by $KMnO_4$ in KHP samples and in soil analysis

Oxidation conditions[a]	Assessments with KHP			Soil analysis
	Acidity effects	Optimization	Mass effect	
Sample mass (mg)	30	30	10, 20, 30, 40 and 50	500
H_2SO_4 concentration (mol L^{-1})	5×10^{-4}, 2.5×10^{-3}, 0.01, 0.025, 0.125, 0.25, 0.5, 1.8, 4.5, and 9.0	0.125, 0.25, and 0.5	0.125, 0.25, and 0.5	0.125
Time (min)	15	15, 30 and 60	30	30
Temperature (°C)	60 and 95	60, 70, 80 and 95	70	70

[a]Oxidation was performed with a mixture of 10.00 mL of 0.2 mol L^{-1} $KMnO_4$ (standard) and 10 mL of H_2SO_4.

heating for the oxidation of OC (Reaction 1). After this time, the tube was set to cool for 15 minutes. The contents were transferred to an Erlenmeyer flask with the subsequent addition of 2.5 mL of 85% w/w H_3PO_4 to avoid Fe^{3+} interference in the visualization of the color change at the endpoint of titration (Reaction 4). With the aid of a burette, the standardized solution of 0.2 mol L^{-1} ferrous ammonium sulfate was added until the solution was bleached (Reaction 2) and the brown solid was completely solubilized (Reaction 3). Excess Fe^{2+} was titrated with 0.02 mol L^{-1} $KMnO_4$ solution until a slightly pink color persisted. The blank analysis did not use KHP or soil samples. The analyses were performed in triplicate.

Reaction 4: $Fe^{3+} + 2H_3PO_4 \rightarrow Fe(PO_4)_2^{3-} + 6H^+$

General equation to TOC determination by the proposed method

Considering that $n^0_{MnO_4^-}$ millimoles of permanganate were added to the system, $n^1_{MnO_4^-}$ millimoles of permanganate reacted with the OC, and $n^2_{MnO_4^-}$ millimoles of permanganate reacted with the added Fe^{2+} ions, and we have the following mass balance:

$$n^0_{MnO_4^-} = n^1_{MnO_4^-} + n^2_{MnO_4^-} \tag{1}$$

If the sample solution contains millimoles of OC and $n^1_{Fe^{2+}}$ millimoles of Fe^{2+} ions that react with the remaining permanganate, based on the stoichiometry of Reactions 1 and 2, Eq. 1 becomes:

$$n^0_{MnO_4^-} = \frac{4n_C}{3} + \frac{n^1_{Fe^{2+}}}{5} \tag{2}$$

For the Fe^{2+} ions added after permanganate oxidation, the mass balance is:

$$n^0_{Fe^{2+}} = n^1_{Fe^{2+}} + n^2_{Fe^{2+}} + n^3_{Fe^{2+}} \tag{3}$$

where: $n^0_{Fe^{2+}}$ is the amount, in mmol, of Fe^{2+} ions added to the solution; $n^1_{Fe^{2+}}$ is the amount, in mmol, of Fe^{2+} ions that react with the remaining permanganate from the OC oxidation; $n^2_{Fe^{2+}}$ is the amount, in mmol, of Fe^{2+} ions that react with MnO_2; and $n^3_{Fe^{2+}}$ is the amount, in mmol, of Fe^{2+} ions that react with the titrant (0.02 mol L^{-1} $KMnO_4$). If $n_{MnO_4^-}$ millimoles of permanganate are needed to titrate Fe^{2+} and, considering the stoichiometry of Reactions 1, 2 and 3, Eq. 3 becomes:

$$n^0_{Fe^{2+}} = n^1_{Fe^{2+}} + \frac{8n_C}{3} + 5n_{MnO_4^-} \tag{4}$$

Replacing Eq. 4 in Eq. 2, to eliminate the term $n^1_{Fe^{2+}}$ results in Eq. 5:

$$5n^0_{MnO_4^-} = 4n_C + n^0_{Fe^{2+}} - 5n_{MnO_4^-} \tag{5}$$

The OC concentration, Fe^{2+} added, and titrant content in the blank analysis are different from the sample. Therefore, we have Eq. 6 for the blank, with the apostrophe (') being used to highlight the blank terms.

$$5n^0_{MnO_4^-} = 4n'_C + n^{0'}_{Fe^{2+}} - 5n'_{MnO_4^-} \tag{6}$$

Equating Eq. 5 to Eq. 6, we have:

$$n_C - n'_C = \frac{n'_{Fe^{2+}} - n^0_{Fe^{2+}} + 5\left(n_{MnO_4^-} - n'_{MnO_4^-}\right)}{4} \tag{7}$$

The term $n_C - n'_C$ corresponds to OC concentration in the sample, in mmol. In this case, we have Eq. 8:

$$n_C - n'_C = \frac{m^{sample}_C}{MM_C} \tag{8}$$

where: m^{sample}_C is the carbon mass in the sample, in mg; and MM_C is the molar mass of carbon (12.0 g mol^{-1}). Replacing Eq. 8 in Eq. 7 and knowing that the quantity of Fe^{2+} ions and titrant spent can be calculated from the respective concentrations and volumes of the solutions used, the TOC in the sample can be determined by Eq. 9:

$$TOC = 3 \times \frac{\left[M_{Fe^{2+}}\left(V^b_{Fe^{2+}} - V^a_{Fe^{2+}}\right) + 5M_{MnO_4^-}\left(V^a_{MnO_4^-} - V^b_{MnO_4^-}\right)\right]}{m_{sample}} \tag{9}$$

where: TOC is the total organic carbon content in the sample, in g kg^{-1}; $M_{Fe^{2+}}$ and $M_{MnO_4^-}$ are the concentrations, in mol L^{-1}, of Fe^{2+} and MnO_4^- ions, respectively; $V^a_{Fe^{2+}}$ and $V^b_{Fe^{2+}}$ are the volumes, in mL, of ferrous ammonium sulfate solution spent in dissolving MnO_2 in the analysis of the blank and the sample, respectively; $V^a_{MnO_4^-}$ and $V^b_{MnO_4^-}$ are the volumes, in mL, of $KMnO_4$ solution spent in the titration of Fe^{2+} ions in the sample and blank analysis, respectively; m_{sample} is the sample mass, in g; and factor 3 is the combination of the molar mass of carbon (12.0 g mol^{-1}) with the stoichiometric term (4) of Eq. 7.
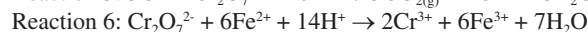
Computation of %OC

The percentage of oxidized carbon (%OC) by the permanganate in the KHP samples was calculated according to Eq. 10:

$$\%OC = \frac{TOC \times MM_{KHP} \times 0.1}{8 \times MM_C} \tag{10}$$

where: %OC is the percentage of oxidized carbon; TOC is the organic carbon content in the sample, in g kg^{-1}; MM_{KHP} is the molar mass of KHP, in g mol^{-1}; MM_C is the carbon molar mass, in g mol^{-1}; 8 is the stoichiometric factor referring to the amount of carbon in the KHP; 0.1 is the conversion factor for the percentage.

Reference method (Yeomans & Bremner)[13]

For the YB method, 500 mg (± 0.1 mg) of soil, 5.00 mL of 0.167 mol L^{-1} $K_2Cr_2O_7$ solution, and 7.5 mL of concentrated H_2SO_4 were added to a 100 mL digestion tube. The tube was placed on the digester block and kept at 170 °C for 30 minutes for the OC oxidation (Reaction 5). After cooling and completing the volume with distilled water to make it 50 mL, 10 mL of 85% w/w H_3PO_4 and 5-8 drops of ferroin indicator solution were added to the tube. The mixture was titrated with 0.2 mol L^{-1} ferrous ammonium sulfate solution (Reaction 6). The blank analysis did not comprise any soil sample addition. Additionally, blank analysis was performed without heating in a digester block to account for the amount of dichromate lost due to heating. Analyzes were performed in quintuplicate.

Reaction 5: $3C + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CO_{2(g)} + 4Cr^{3+} + 8H_2O$
Reaction 6: $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

RESULTS AND DISCUSSION

The acidity effect on KHP oxidation

The effect of acidity on the determination of the %OC of KHP by $KMnO_4$ was evaluated by varying the concentration of H_2SO_4 from 5.0×10^{-4} to 9.0 mol L^{-1} at temperatures of 60 °C and 95 °C and 15 minutes of reaction (Table 1). The most promising H_2SO_4

concentration for KHP oxidation was 0.25 mol L^{-1} ($-logC_{H_2SO_4} = 0.6$), which provided %OC values of 91% ($\pm$ 4%) and 104.8% ($\pm$ 1.6%) at 60 °C and 95 °C, respectively (Figure 1). However, adequate %OC values were also obtained at H$_2$SO$_4$ concentrations: of 0.125 mol L^{-1}, 95% ($\pm$ 7%), at 60 °C; of 0.5 mol L^{-1}, 114% ($\pm$ 9%) at 95 °C; and 1.8 mol L^{-1}, 91% ($\pm$ 12%) at 95 °C.
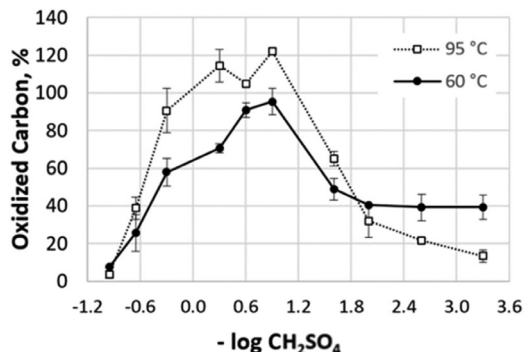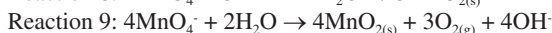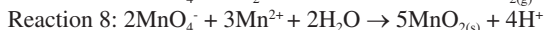

Figure 1. *Percentage of oxidized carbon (% CO) in KHP as a function of the negative logarithm of the sulfuric acid molar concentration (logC$_{H_2SO_4}$) at temperatures of 60 °C and 95 °C (N = 3)*

Figure 1 shows that the oxidation of KHP should be carried out under moderate acidity conditions for greater accuracy. The low values of %OC obtained in a medium of lower acidity may be caused by the insufficient amount of H$^+$ ions for Reaction 1. In a medium of greater acidity, low values of %OC are also found. In this case, it is necessary to consider the following discussion.

A gradual increase in MnO$_2$ formation was observed in the blank oxidation with an increase in acidity, suggesting that MnO$_2$ is also produced by a parallel reaction to the oxidation of KHP by KMnO$_4$. The increase in MnO$_2$ formation was visual and confirmed by the need to add a greater volume of ferrous ammonium sulfate solution in the system after oxidation with KMnO$_4$. Diluted solutions of KMnO$_4$ in H$_2$SO$_4$ are relatively stable. However, KMnO$_4$ reacts with water in more concentrated solutions, producing Mn^{2+} (Reaction 7).[59] Mn^{2+} ions, in turn, considerably increase the degradation of KMnO$_4$, producing MnO$_2$ (Reaction 8), which catalyzes the reaction of KMnO$_4$ with water,[59] forming more MnO$_2$ (Reaction 9). Hence, greater formation of MnO$_2$ was observed when using more concentrated solutions of H$_2$SO$_4$. Therefore, under conditions of higher acidity, these parallel reactions of KMnO$_4$ seem to be a priority in relation to its reaction with KHP in the investigated time (15 min), which decreases the %OC recovered (Figure 1).

Reaction 7: $2MnO_4^- + 5H_2O + 6H^+ \rightarrow 2Mn^{2+} + 5/2O_{2(g)} + 8H_2O$
Reaction 8: $2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_{2(s)} + 4H^+$
Reaction 9: $4MnO_4^- + 2H_2O \rightarrow 4MnO_{2(s)} + 3O_{2(g)} + 4OH^-$

The %OC values greater than 100% observed in Figure 1 may be due to the MnO$_2$ produced in the oxidation of OM (KHP) (Reaction 1), which catalyzes the reaction of KMnO$_4$ with water (Reaction 9).[59] The reaction of KMnO$_4$ with water in the blank analysis does not occur in the same proportion as in the sample analysis because of the absence of OM, which was confirmed by the low formation of MnO$_2$ observed in the blank. Consequently, the %OC became greater than 100%.

Optimization of reaction conditions for KHP oxidation

As the %OC values were satisfactory at H$_2$SO$_4$ concentrations of 0.125, 0.25, and 0.5 mol L^{-1} (Figure 1), the effect of oxidation time

(15 to 60 min) and temperature (60 at 95 °C) in the oxidation of KHP by KMnO$_4$ were assessed for these concentrations (Table 1, Figure 2).
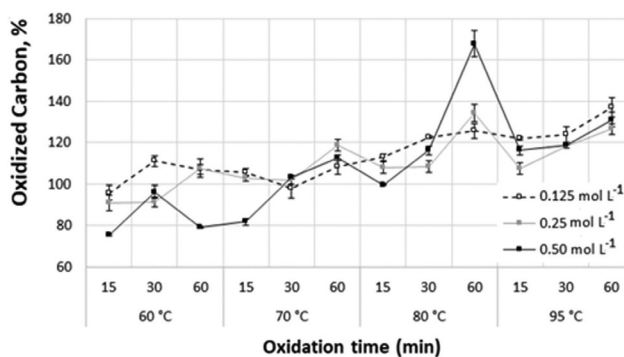

Figure 2. *Percentage of carbon oxidized by KMnO$_4$ in KHP, under different concentrations of H$_2$SO$_4$ (0.125, 0.25 and 0.5 mol L^{-1}), temperatures (60, 70, 80 and 95 °C) and reaction times (15, 30 and 60 min) (N = 3)*

Since the desirable OC oxidation is 100%, the reaction conditions that provided relative errors (*e*) of up to 3.0% (|*e*|≤3.0%) for the KHP oxidation were: 0.125 mol L^{-1} H$_2$SO$_4$, 70 °C and 30 min (1.9%); 0.25 mol L^{-1} H$_2$SO$_4$, 70 °C and 15 min (2.6%); 0.25 mol L^{-1} H$_2$SO$_4$, 70 °C and 30 min (2.0%); 0.5 mol L^{-1} H$_2$SO$_4$, 70 °C and 30 min (3.0%); and 0.5 mol L^{-1} H$_2$SO$_4$, 80 °C and 15 min (0.4%) (Figure 2). The coefficients of variation across the conditions investigated were less than 5.0%.

Figure 2 shows a trend of obtaining higher %OC with increasing time and temperature of OM oxidation. All %OC values at temperatures of 80 °C and 95 °C were statistically higher than 100% (Student's t-test; $\alpha = 0.05$; one-tailed), except for oxidation with 0.5 mol L^{-1} H$_2$SO$_4$ at 80 °C for 15 minutes. Such behavior seems to be related to the catalytic effect of MnO$_2$ on the reaction of water with KMnO$_4$ (Reaction 9). Hence, the oxidation of OM with KMnO$_4$ at 80 and 95 °C is not recommended.

KHP mass effect on %OC

The assessment of the KHP mass effect on the %OC value determined experimentally was motivated by the vast number of parallel reactions that can occur during the OM oxidation with permanganate. Other motivation factors were the different oxidation states that manganese could acquire when reduced and possible favoritism of a parallel reaction caused by some excess reagents or by the accumulation of some intermediate reaction.

The best results were obtained when using 10, 20 and 30 mg of KHP with 0.125 mol L^{-1} H$_2$SO$_4$, for which the %OC values were 96% ($\pm$ 3%), 96.9% ($\pm$ 0.5%) and 94.8% ($\pm$ 1.4%), respectively (Figure 3). Good values were also obtained with 0.25 mol L^{-1} H$_2$SO$_4$ together with 20 mg of KHP, 94.0% ($\pm$ 1.7%) and 0.5 mol L^{-1} H$_2$SO$_4$ combined with 40 mg of KHP, 94% ($\pm$ 2%) (Figure 3).

The oxidation of OM by KMnO$_4$ using 0.5 mol L^{-1} H$_2$SO$_4$ and 10, 20, and 30 mg of KHP was overestimated as the %OC varied from 120% to just over 210% (Figure 3), which may be related to the parallel KMnO$_4$ reaction with water (Reaction 9). Across the three acidity conditions tested, the %OC values were lower for the masses of 40 and 50 mg of KHP. This behavior is due to the amount of KMnO$_4$ used, which was insufficient to react completely with the OC of 40 and 50 mg of KHP, based on the stoichiometry of Reaction 1. The agreement between the theoretical and experimental %OC values under the conditions in that there was no substantial influence of parallel reactions (10 – 50 mg of KHP, in 0.125 and 0.25 mol L^{-1} H$_2$SO$_4$ and 40 – 50 mg of KHP, in 0.5 mol L^{-1} H$_2$SO$_4$, Figure 3) corroborate
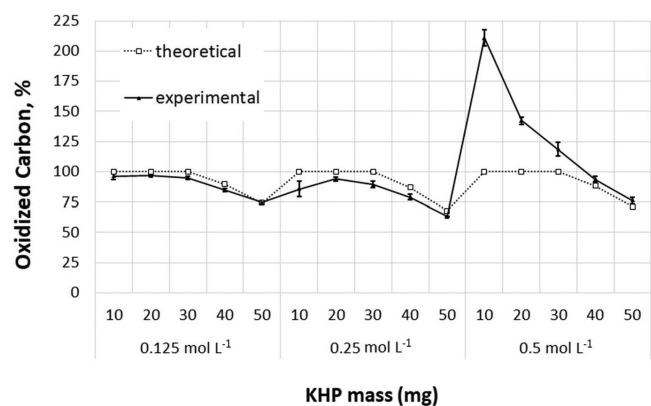
Figure 3. Theoretical and experimental percentages of oxidized carbon in the reaction of KHP with KMnO$_4$ using different H$_2$SO$_4$ concentrations (0.125, 0.25 and 0.5 mol L^{-1}) and KHP masses (10, 20, 30, 40 and 50 mg) (N = 3)

the proposal of this work, in which the primary reaction between OC and KMnO$_4$ involves the formation of MnO$_2$ (Reaction 1) confirming its feasibility as an oxidant to TOC determination.

Soil TOC determination

The oxidation of SOM with KMnO$_4$ was carried out at 70 °C for 30 min, using 0.125 mol L^{-1} H$_2$SO$_4$ (Table 1), as these are the best conditions observed for the oxidation of KHP (Figure 2 and Figure 3). Although differences were observed between the proposed method and YB, for three types of soil (Table 2), these differences do not invalidate the method. Pereira *et al.*[28] also found a significant relative error ranging from 67% to 129% between TOC determined with EA and YB in *cambissolo* samples.

In fact, the nature of the matrix and environmental characteristics affect the reliability of different methods for measuring carbon content.[27] Different soils present diverse sorption properties (of inorganic and organic particles) as well as various OM protection mechanisms within the aggregates that contribute to the storage of OM and its lability.[60] The organic matter quality can be one of the contributors to the divergences observed in the methods.[61] Hence, consistent measurements among different methods, matrices and applications can enable further trend comparisons.[27] Moreover, the differences among methods can be corrected by the use of correction factors (Table 2), calculated according to Eq. 11:

$$f = \frac{TOC_{Ref}}{TOC} \qquad (11)$$

where: f is the correction factor; TOC_{Ref} and TOC are the organic carbon contents obtained by the reference and proposed methods (in g kg^{-1}), respectively.

Correction factors have been widely used in the routine analysis of soil samples,[26,28,62] as SOM can be highly complex, ranging from

compounds such as simple sugars and amino acids to acids humic and fulvic. Thus, in some instances, the oxidation of OC may not be complete justifying the use of correction factors even in official methods that have been used for several decades, such as YB and WB.[26,28,62] Therefore, the differences observed in the results in Table 2 do not constitute a problem capable of disqualifying the proposed method since its potential was proven in the KHP analysis. In this case, the observed deviations for a specific type of soil can be corrected, as usual, using correction factors.

Concerning the precision of the methods (Table 2), it was observed that the proposed method was statistically similar to the reference method (YB) under the one-tailed F-test (α =0.05), except for the *gleissolo*, which was superior. These results display the similarity between the two methods, indicating that both can be applied interchangeably in the TOC determination.

Feasibility of the proposed method to be applied in carbon dynamics studies

Due to the importance of SOC to the sustainability of the ecosystems, its determination has become essential as a soil health indicator because it reflects soil organic matter dynamics.[4,8,14] In order to quantify and evaluate soil health and quality, adequate indicators are required.[8,53] Indicators suitable for soil health evaluation must be rapid and straightforward, cost-effective, sensitive to management, and present low analytical variability.[8,53]

For the United States Department of Agriculture – Natural Resources Conservation Services, both dry combustion (EA) and wet oxidation are considered candidate indicator methods for OC. However, the EA is regarded as a more suitable option since it meets all criteria except for the minimal infrastructure and investment, which is partially met due to the high cost of acquiring a carbon analyzer. At the same time, the major drawbacks of the wet oxidation (YB) method are the hazardous waste and its disposal.[8]

The analysis of 100 soil samples through the method proposed in this study could reduce K$_2$Cr$_2$O$_7$ consumption by 49 g (Table 3). The Cr^{6+} has high carcinogenic, mutagenic, reproductive, dermal, and inhalation toxicity potential.[63] Therefore, although Cr^{6+} is reduced to Cr^{3+} (less toxic) at the end of the analysis, handling K$_2$Cr$_2$O$_7$ exposes the analyst to unnecessary risks that could be avoided by using a safer oxidant (e.g., KMnO$_4$).

Another benefit of the method is the reduction of H$_2$SO$_4$ used. The proposed method could consume 186 mL of concentrated H$_2$SO$_4$ for 100 soil samples analyzed compared to 950 mL of acid used by the YB method, meaning a reduction of 80.4% of H$_2$SO$_4$ consumption (Table 3). As security agencies in several countries control sulfuric acid purchases, reducing its demand can also optimize its use in a lab routine.[35-38] The advantages of the method enable an environmentally friendly method and the application in any analytical laboratory without demanding high economic resources as required by the EA. This context supports research settings where resources are limited by suggesting a method that

Table 2. Total organic carbon content, in g kg^{-1}, and correction factors obtained in soil analysis by the reference method (YB) and the proposed method

Brazilian[57]/ Soil Taxonomy[58] equivalent	Total organic carbon content (g kg^{-1})		Error (%)	Factor	F-value[a]
	Reference method	Proposed method			
Chernossolo / Molisols	24.0 ± 0.1	23.8 ± 0.3	0.8	0.992	8.8
Latossolo / Oxisols	17.3 ± 0.5	19.3 ± 0.6	-12	1.12	1.3
Gleissolo / Entisols (poor drainage conditions)	8.7 ± 0.4	7.2 ± 0.1	17	0.828	42
Cambissolo / Inceptisols	8.9 ± 0.2	5.8 ± 0.2	35	0.652	2.3

[a]F critical value = 19 (α = 0.05).

Table 3. Comparison between the proposed and the YB methods used for the determination of organic carbon in soils

Conditions	Proposed method	YB method
Oxidizing agent	$KMnO_4$	$K_2Cr_2O_7$
H_2SO_4 amount	10 mL / 0.125 mol L^{-1}	7.5 mL / concentrated
Oxidation time	30 min	30 min
Oxidation temperature	70 °C	170 °C
Oxidizing agent mass / 100 soil samples	65 g	49 g
Concentrated H_2SO_4 volume / 100 soil samples[a]	186 mL	950 mL

[a]Considering OM oxidation reaction and the preparation of the ferrous ammonium sulfate solution.

is simple, fast, and inexpensive as the YB with fewer consumables and hazardous waste generation.

CONCLUSIONS

This study shows that $KMnO_4$, when reduced to MnO_2, has a similar potential to $K_2Cr_2O_7$ for the determination of TOC. The advantage of this new methodology involves a lower consumption of H_2SO_4 and a low temperature to oxidize the OM. Changing the oxidant and reaction conditions brings less risk to health and the environment. For the method to reach a broader application, it is recommended to analyze a larger number of soil types and determine the conversion factors by comparing the results obtained with those of the reference method (EA).

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