

Gravimetric Determination of Soil Organic Matter

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ABSTRACT

Studies were carried out to evaluate a gravimetric method for the determination of soil organic matter by the mass loss at 300°C. The gravimetric method was compared with Walkley-Black, using several Brazilian soils with variable chemical and physical properties. Gravimetric method was positively correlated with Walkley-Black method with the following linear regression equation: $y = 3.72x + 0.29$, $r = 0.94$. The angular coefficient 3.72 for tropical soils was greater than those reported in the literature for temperate soils (from 1.68 to 2.13). The difference was due to greater oxidation degree of the organic matter. When compared with Walkley-Black method, gravimetric technique showed certain distinct advantages such as no environmental contamination with Cr^{6+} and improved laboratory safety eliminating the use of concentrated sulfuric acid.

Key words: organic carbon, thermogravimetry, soil analysis.

INTRODUCTION

The importance of soil organic matter on physical, chemical, and biological properties of soil with implications on erodibility, nutrient cycling, water storage and resultant soil productivity is well established. These efficiencies affect both crop production and natural resources sustainability, and they are mutually reinforcing.

Soil organic matter is usually evaluated through determination of organic carbon. Several techniques have been developed for measuring soil organic carbon, such as Walkley-Black (WB) (Jackson, 1982), gravimetry (Ball, 1964; Ben-Dor & Banin, 1989), thermogravimetry (Wendlandt, 1986; Beltran et al., 1988), and chromatography (Dean, 1974). The Walkley-Black method is based on organic carbon oxidation by Cr^{6+} in the presence of concentrated H_2SO_4 . The excess of Cr^{6+} is titrated with Fe^{2+} or determined by spectrophotometry with Cr^{3+} formation. Gravimetric and thermogravimetric methods are based on mass loss, respectively, by incineration and heating.

The majority of Brazilian soil laboratories uses the WB method due to its higher speed and simple instrumentation. However, the disadvantages of the WB method are the use of concentrated H_2SO_4

and the presence of Cr^{6+} . Gravimetric determination of soil organic matter was used before WB method. However, it was abandoned due to low analytical velocity and difficulty for automation in the laboratory. The objectives of the present study were to re-evaluate the gravimetric method for routine determination of soil organic carbon and to determine the organic carbon/organic matter (OC/OM) ratio of the tropical soils.

MATERIALS AND METHODS

Thermogravimetric method (TGA) – ten milligrams of soil sample ($< 200 \mu\text{m}$) were used for analysis in a TGA Dupont instrumentation, model 5000. Heating increment was $15^\circ\text{C min}^{-1}$ in the interval from 25 to 600°C with atmosphere air. Brazilian soil samples were selected containing organic matter varying from 10 to 100 g kg^{-1} . The organic matter was determined by the mass loss in the interval from 110 to 420°C in the thermogravimetric curve.

Differential scanning calorimetry method (DSC) – one hundred milligrams of soil samples

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(< 200 μm) were used for analysis in a DSC DuPont instrumentation model 2000. Heating increment was $15^\circ\text{C min}^{-1}$ in the interval from 25 to 600°C in atmosphere air and N_2 .

Walkley-Black method (WB) – one gram of soil sample was transferred to 250ml Erlenmeyer and added 10ml of 1N $\text{K}_2\text{Cr}_2\text{O}_7$ and 10ml of concentrated H_2SO_4 . After 30 minutes, 50 ml of deionized water, 3ml of concentrated H_3PO_4 and 0,5 ml of 1% defenilamina indicator were added. Then, titrated slowly with 1N FeSO_4 solution up to a green color end point.

Gravimetric method (GM) – one gram of soil sample was transferred to 10ml becker and incinerated in an electric muffle for 1 hour at 250, 300, 350, and 400°C . Incineration time of 0.5, 1.0, 2.0, and 4.0 hours at 300°C was also evaluated.

Total organic carbon (TOC) – Total soil carbon was oxidized to CO_2 at 800°C in atmosphere air, and determined by thermic conductivity.

RESULTS AND DISCUSSION

Thermogravimetric diagram for a red latossol with 19.8g kg^{-1} of carbon is shown in Figure 1.

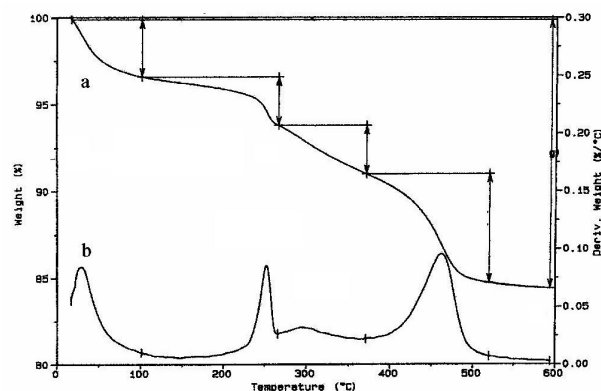


Figure 1 - Thermogravimetric diagram for red latossol with 19.8g kg^{-1} of carbon in atmosphere - air 100mL min^{-1} . (a) relative mass loss, (b) differential mass loss.

The diagram showed four characteristic regions in the interval from 25 to 600°C . The first region (< 100°C) showed that mass loss (0.383mg) was mainly due to water volatilization; in second region ($200\text{--}280^\circ\text{C}$), the mass loss (0.323mg) was mainly due to decomposition of organic matter, mainly carboxylic and phenolic functional groups of the humic and fulvic acids and hydrocarbon compounds. In the second region the

mass loss could also be due to release of low molecular weight organic compounds (Wendlandt, 1986; Beltran et al., 1988). The third region ($270\text{--}370^\circ\text{C}$) had the mass loss (0.324mg) mainly due to carbon oxidation of the organic matter ($\text{R-CH} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$). In fourth region ($380\text{--}530^\circ\text{C}$), the mass loss (0.726mg) was mainly due to dehydroxilation of metallic hydroxides ($\text{M-OH} \rightarrow \text{MO} + \text{H}_2\text{O}$, where $\text{M} = \text{Al, Fe, Mn}$ and other metals).

Calorimetric diagrams in atmosphere air and in N_2 for the interval between 25 to 600°C are shown in figures 2 and 3, respectively.

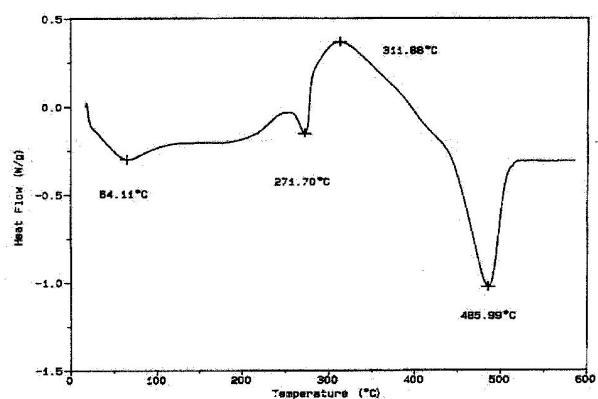


Figure 2 - Calorimetric diagram in atmosphere air 100ml min^{-1} .

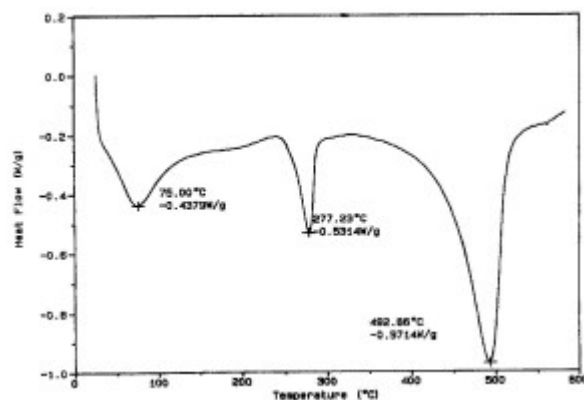


Figure 3 - Calorimetric diagram in atmosphere N_2 100mL min^{-1} .

The first endothermic peak appeared at 60 and 75°C in air atmosphere and N_2 , respectively, corresponding to the loss of water molecules observed in the thermogravimetric curve (Figure 1). The second endothermic peak was observed at 271.7 and 277.23°C in air atmosphere and N_2 , respectively corresponding to dehydroxilation and

decarboxilation of organic compounds. The greater peak for the N₂ in relation to air, suggested a partial oxidation of organic matter. The decomposition of organic matter caused a peak at 475 °C in N₂ only. The exothermic peak between 275 and 470°C in air atmosphere only corresponded with the mass loss observed in the thermogravimetric diagram > 270°C (Figure 1). Both thermogravimetric and calorimetric diagrams suggested that thermic decomposition of organic matter in soil occurred between 200 and 280°C and the oxidation of carbon between 270 and 420°C. The WB method was highly correlated with mass loss by incineration at 250, 300, 350, and 400°C, presenting the following linear regression equations, respectively: $y = 3.369x + 0.2716$, $r = 0.923$; $y = 3.720x + 0.2914$, $r = 0.937$; $y = 4.054x + 0.5046$, $r = 0.934$ and $y = 4.298x + 0.5357$, $r = 0.933$.

Figure 4 presents the relationship between WB and incineration at 300°C methods. The mass loss by thermogravimetry (110 and 420°C) and by incineration at 300°C was also highly correlated ($y = 1.0556x + 0.1632$, $r = 0.986$). The mass loss by incineration (300°C) for 0.5, 1.0, 2.0, 4.0, and 18.0 h was exactly the same for all times. These results showed that the soil organic matter was completely decomposed at 300°C for 30 minutes of incineration.

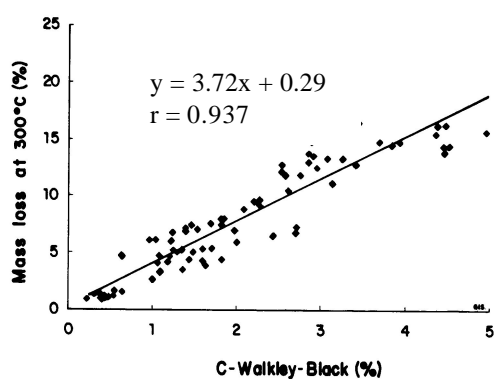


Figure 4 - Correlation between WB and incineration at 300°C.

The WB and incineration at 300°C methods were compared with soil organic carbon oxidized by 30% H₂O₂ (Table 1). The H₂O₂ oxidized more than 80% of the total organic carbon. The relationships between WB and incineration methods before and after H₂O₂ oxidations was, respectively: $y =$

$3.620x + 4.562$, $r = 0.861$ and $y = 18.04x + 14.42$, $r = 0.760$. The increase in the angular coefficient from 3.62 to 18.04 suggested an increase in the oxidation of residual soil organic carbon. The WB method was also highly correlated with total organic carbon ($y = 0.918x + 0.368$, $r = 0.992$). These results showed high precision of the WB method, and the possible interferences by Cl⁻ and Fe²⁺ ions are negligible.

Table 1 - Organic matter determination by incineration at 300°C and carbon by WB in soils before and after oxidation by 30% H₂O₂.

Soil N ^o	Before oxidation		After oxidation	
	WB	Incineration	WB	Incineration
	----- g kg ⁻¹ -----			
1	44.6	138.4	5.5	98.2
2	43.6	154.4	7.2	106.8
3	10.5	60.1	5.0	49.2
4	13.7	34.3	4.6	25.4
5	33.5	147.3	8.1	124.5
6	14.0	0.5	2.7	47.9
7	18.3	43.2	2.2	8.3
8	38.4	145.2	6.1	108.3
9	27.2	72.2	3.0	20.2
10	21.1	58.6	2.3	14.8
11	28.6	137.2	4.4	98.4
12	22.1	94.7	2.9	67.7
13	25.4	127.0	4.0	95.8
14	32.0	148.6	5.0	109.1
15	16.1	41.6	4.1	19.7

Determinations of organic matter in several Brazilian agriculture soils by WB and mass loss at 300°C methods showed high correlation (Figure 4). The angular coefficient of 3.72 was much higher than those reported in the literature. Studies with different soils where WB method was compared with thermogravimetric method showed angular coefficient of 2.13 (Dean, 1974), 1.68 (Giovannini et al., 1985), 2.05 (Ben-Dor & Banin, 1989) and 1.724 (Jackson, 1982). The greater angular coefficient of the Brazilian soils (3.72) was probably due to higher oxidation degree of the organic matter. In other words, the organic molecules of the tropical soils presented a greater number of functional groups with oxygen atoms, such as R-COOH, R-C=O, R-COH, and others. Therefore, for the Brazilian soils the estimation of

soil organic matter could be obtained by determining the mass loss at 300°C and solving the linear regression [$x = (y - 0.29) / 3.72$]. Where x = organic carbon and y = mass loss at 300°C. This factor was higher than that used in the majority of brazilian soil laboratories (Raij & Quaggio, 1983). It was important to note that the factor used in the brazilian soil laboratories is the same suggested by Jackson (1982) for north american soils. Determinations of organic carbon by WB and thermogravimetric methods in soil samples used in the international soil analysis program coordinated by the Wageningen University showed the following linear regression $y = 1.55x + 6.66$ $r = 0.94$. Soil samples coefficient was 1.55 which was closer to those reported in the literature (Ball, 1964; Jackson, 1982; Ben-Dor & Banin, 1989). These results suggested that the higher organic matter/organic carbon (OM/OC) ratio of the brazilian soils was due to higher oxidation degree of the organic matter. Determinations of organic carbon from organic residues by WB and incineration at 300°C methods were also highly correlated ($y = 1.606x - 0.1704$, $r = 0.995$). The regression coefficient of 1.606 was closer to 1.680 found for sewage sludges (Giovannini et al., 1985).

CONCLUSIONS

Gravimetric method could be used for determination of organic matter in routine soil analysis with advantages of eliminating Cr and concentrated H₂SO₄. Tropical brazilian soils presented higher OM/OC relationship.

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RESUMO

Avaliou-se o método de determinação gravimétrica da matéria orgânica do solo pela perda de massa por incineração a 300°C e comparou-se com o carbono determinado pelo método Walkley-Black. Os dois métodos foram correlacionados positivamente com a seguinte equação de regressão linear: $y = 3,720x + 0,2914$. $r = 0,937$. O coeficiente, 3,720 foi maior do que os encontrados na literatura, que variaram de 1,68 a 2,13. Esta diferença foi atribuída ao maior grau de oxidação da matéria orgânica dos solos das regiões tropicais. O método de incineração é aplicável para determinação do C do solo em rotina. O método não contamina o meio ambiente com metal tóxico (Cr⁶⁺) e não oferece riscos aos analistas com o uso de ácido sulfúrico concentrado.

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