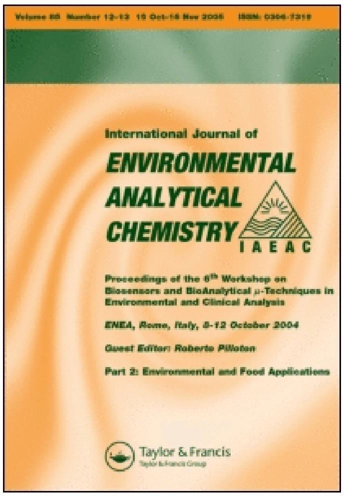

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COMPARATIVE STUDY OF TITRIMETRIC AND GRAVIMETRIC METHODS FOR THE DETERMINATION OF ORGANIC CARBON IN SOILS

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Fourty seven soil samples were collected from agriculture fields at two depths (0–15 cm and 15–30 cm). The samples were analysed to determine the total organic carbon TOC (using the dry combustion reference method), the organic carbon OC (using wet acidified $Cr_2O_7^{2-}$ and MnO_4^- oxidation) and organic matter OM (using loss on ignition). A comparison between the TOC and each of OC and OM were carried out using regression analysis. This analysis reveals an excellent linear relation between the results of wet acidified $Cr_2O_7^{2-}$ oxidation and dry combustion with a mean conversion factor of 1.109, while a new conversion factor of 1.841 between wet acidified MnO_4^- oxidation and dry combustion is proposed. Also, regression analysis reveals that the linear relation between loss on ignition and the dry combustion reference method gives a stronger intercept ($a > 0$), indicating that these are less related (the traditional equation by Walkley and Black assumed the intercept $a = 0$). The stronger intercept ($a > 0$) in our study reflects the removal of non-organic soil constituents during ignition. This linear relation was improved by inclusion of clay percentage as an independent variable using multiple regression analysis.

KEY WORDS: Soil, organic carbon, CHN analyzer.

INTRODUCTION

Analytical methods for the determination of the organic carbon (OC) in soils rely on the titrimetric measurements which involve acid hydrolysis of organic materials in the presence of an oxidant. Most of the determined organic carbon by titrimetric methods used dichromate as an oxidant[1,2]. The results showed that recoveries of organic carbon were of 97% from twenty two soil samples of varied textures. The failure to obtain 100% recoveries was attributed to the fact that the oxidation condition oxidized only a part of the organic carbon. If the total organic carbon (%TOC) is desired, the organic carbon (%OC) is multiplied by a conversion factor (the inverse of the fraction oxidized). Recently, a micro combustion method was developed to overcome the limitations of the titrimetric method. Nelson and Sommers[3] re-examined the relationship between % OC and % TOC. They reported an average conversion factor of 1.26, while Walkley and Black[4] and Amacher *et al.*[5] suggested an average conversion factor of 1.32 and 1.41, respectively. Since organic matter (OM) has conventionally assumed to contain on average 58% organic carbon, organic carbon figures have normally converted to organic matter by multiplying by a factor of 1.72[4]. Loss on ignition is not a true measure of organic matter because at the temperature ashing some bound water is lost from the clay minerals. This error is also more serious for soils of low organic content. Howard[6] showed that no specific factor is suitable for all soils to convert OC to TOC and TOC to OM, due to the differences in chemical and physical characters of different soils. Unfortunately, all the past efforts for the determination of the conversion factor were applied only to 10–20 soil samples (collected from Britain and British Columbia)[1,2].

In the present study, fourty seven soil samples from the Sohag area (upper Egypt) were analysed for organic carbon by oxidation with dichromate and permanganate in acid medium and compared with dry combustion as a reference method. The loss on ignition was also compared with the dry combustion method. The comparison enabled the inter-conversion of organic carbon and total organic carbon, and of organic matter and total organic carbon.

EXPERIMENTAL

Sampling

Fourty seven soil samples were collected in January 1992 from twenty four different locations at two depths (0–15 and 15–30 cm) in the Sohag area (upper Egypt). Thirteen sites were located at the west side while the rest from the east along the River Nile to represent all the agriculture fields in the Sohag region.

Soil samples were air- and oven-dried, then passed through a stainless steel sieve (2 mm), to be prepared for the determination of organic carbon and organic matter contents. The samples were ground with ceramic mortar and sieved to separate a particle size fraction (< 150 μm) for the determination of total organic carbon. Then, they were stored in polyethylene bottles.

Procedures

All reagents used were obtained from Merck. The soil clay content was measured with the standard pipette method[7]. The pH value was measured in 1:1 (soil:water) suspension using in Orion pH electrode. Carbonate content was measured with standard HCl and back titration of unused with standard NaOH using pH curve[7]. Organic carbon content (OC) was determined volumetrically by $Cr_2O_7^{2-}$ (Tinsley method)[1] and MnO_4^- [7] in acid medium. The content of total organic carbon (TOC) was measured by a CHN elemental analyzer (Model, Leco CHN 600), after decarbonated soil samples with dilute HCl. Organic matter (OM) was estimated by loss on ignition at two different temperatures (450°C and 600°C, after heating 6 hours in a muffle furnace). To check the accuracy, measurements of pH and CO_3^{2-}, OC and OM contents were replicated three times. The standard samples were checked after every four measurements in determining the total organic carbon (TOC).

RESULTS AND DISCUSSION

Soil properties

Table 1 shows that the mean content of TOC (reference method) is higher than OC (wet acidified dichromate oxidation) for the whole samples in the study area. This is probably

Table 1 Mean value, standard deviation and range for pH, clay, dry combustion (an estimator of total organic carbon, TOC), wet acidified with dichromate and permanganate (an estimator of organic carbon, OC) and loss on ignition (an estimator of organic matter, OM) contents in the Sohag region.

		No	$\bar{x}$	*Sd*	*Range values*
pH		47	8.29	0.23	7.65 – 8.5
CO_3^{-2}	(%)	47	6.87	0.95	3.6 – 7.9
Clay	(%)	47	19.67	4.64	10 – 31
TOC	(%)	47	1.480	0.25	0.95 – 2.16
OC $Cr_2O_7^{2-}$	(%)	47	1.264	0.22	0.22 – 1.92
OC MnO_4^-	(%)	47	0.499	1.09	0.23 – 0.76
Ign.450°C	(%)	47	8.88	1.11	5.60 – 10.8
Ing.600°C	(%)	47	8.98	1.12	5.62 – 10.9

No = number of samples, $\bar{x}$ = mean value,
Sd = standard deviation, Ign. = loss on ignition

due to the incomplete oxidation of the carbonaceous materials, particularly lipids and proteins by chromic acid. This error is reduced by inclusion of a correction factor[8]. The results also show that the mean content of OC determined by wet acidified dichromate is higher than %OC determined by wet acidified permanganate oxidation (Table 1). This is probably attributed to the fact that the soil samples in the Sohag area contain high values of reduced compounds such as iron (II) and manganese oxides ((7.16% and 0.122%, respectively)[9]. Moreover, Table 1 shows that the content of OM measured at 450°C and 600°C by loss on ignition is higher than TOC measured by dry combustion. This may be due to the mass loss at high temperatures of non-organic materials such as carbonates (CO_2 release) and clay minerals (loss of water from hydroxyl groups in sesquioxide and octahedral sheets in phyllosilicate layers).

Conversion factors in Egyptian soils

It is clear from the above mentioned results that the organic carbon (OC) is partially oxidized using the titrimetric titration. The dry combustion reference method gives an actual measurement of total organic carbon (TOC). Therefore, titrimetric methods require an empirical factor to convert OC to TOC. From Figures 1 and 2 it is concluded that the relationships between TOC% (reference method) and OC% (wet acidified $Cr_2O_7^{2-}$ and MnO_4^- oxidation) could be described as follows:

	$[r^2]$	$[n]$	
$[TOC] = 0.088 + 1.109\,[OC]_{Cr_2O_7^{2-}}$	0.93	47	(1)
$[TOC] = 0.559 + 1.841\,[OC]_{MnO_4^-}$	0.64	47	(2)

where $[r^2]$ is the correlation coefficient and [n] the number of samples. Equations 1 and 2 suggest a conversion factors of 1.109 (with recovery factor 91%) and 1.841 (with recovery factor 54%), respectively. These values are compared with the value of 1.03 (with recovery factor 97%) recommended by Tinsley[1] and with the most common value

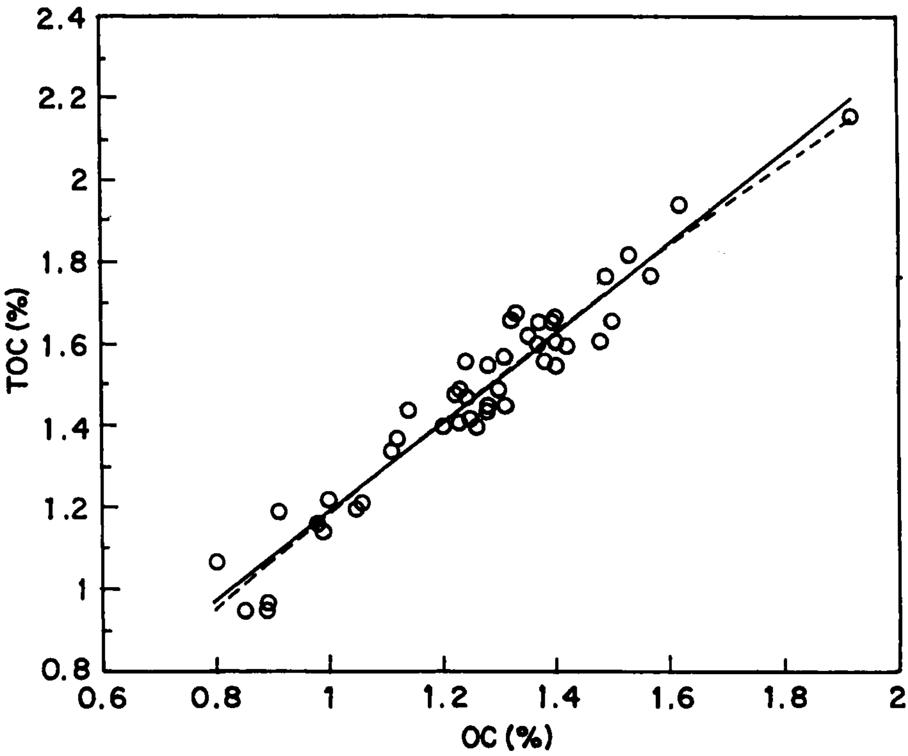

Figure 1 Relationship between dry combustion (an estimator of total organic carbon, TOC) and wet acidified by $Cr_2O_7^{2-}$ (an estimator of organic carbon). The dashed and solid lines represent linear and quadratic fits, respectively.

of 1.32 (with recovery factor 76%) recommended by Walkley and Black[4]. The low recovery factor in equation 2 (wet acidified permanganate oxidation) is probably attributed to the existence of large amounts of reduced compounds in soil samples. However, the intercept of 0.088 and 0.559 in equations 1 and 2, respectively, are significantly different from zero. Also, the multiple regression analysis between TOC and both OC and clay content are shown as follows:

$$[TOC] = 0.0977 + 1.101\ [OC]_{Cr_2O_7^{2-}} + 0.0005\ [clay] \qquad (3)$$

$$[TOC] = 4.754 + 1.846\ [OC]_{MnO_4^-} + 0.0049\ [clay] \qquad (4)$$

Comparison between linear (equations 1 and 2) and multiple regression (equations 3, 4) indicates that the content of clay has a low significant effect on the conversion factor values. The possibility of fitting a curvilinear relation is expressed as follows:

	$[r^2]$	$[n]$	
$[TOC] = -0.082 + 1.082\ [OC]_{Cr_2O_7^{2-}} - 1.387\ [OC]^2_{Cr_2O_7^{2-}}$	0.932	47	(5)
$[TOC] = 0.399 + 2.511[OC]_{MnO_4^-} - 0.671\ [OC]^2_{MnO_4^-}$	0.64	47	(6)

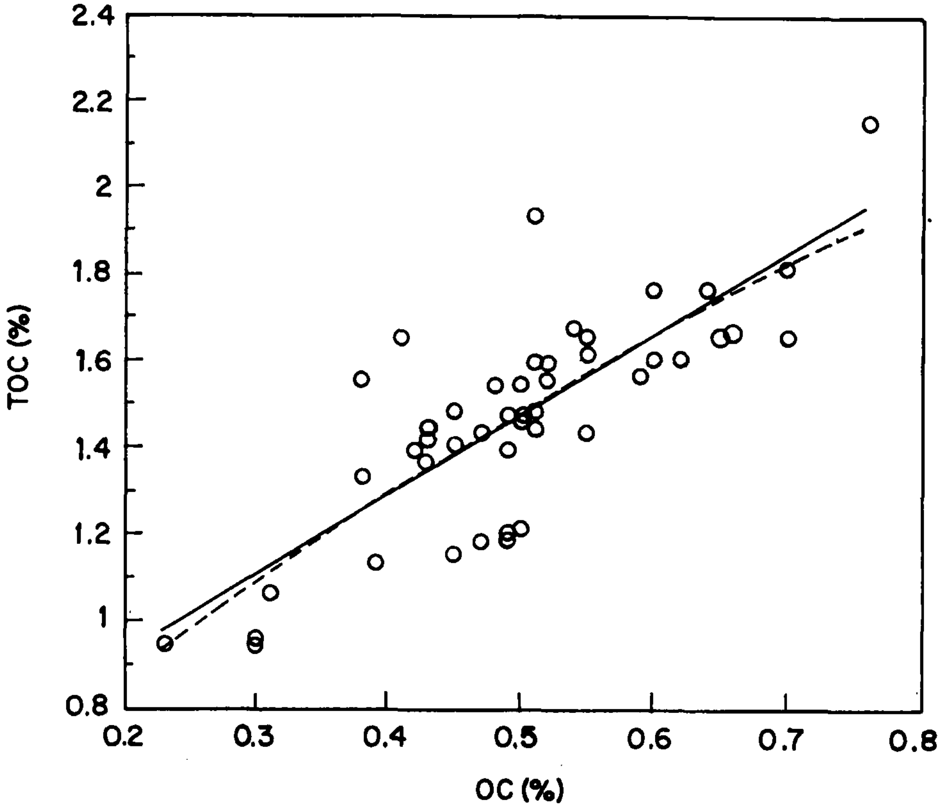

Figure 2 Relationship between dry combustion and wet digestion by acidified MnO_4^-. The dashed and solid lines represent linear and quadratic fits, respectively.

It is clear from Figures 1 and 2, the quadratic curves pass close to the origin, with intercepts of –0.082 and 0.399, respectively. However, as the quadratic term $[OC]^2$ in equations 5 and 6 appear to have no direct physical interpretation, the linear relations (equations 1 and 2) are preferred on physical grounds.

The results from the loss on ignition method is a rough indication of the content of organic matter present in soil. Therefore, loss on ignition is not a true measure of OM because at the temperature of ashing some pound water is lost from clay minerals and is included in the overall loss. The choice of a suitable temperature for soil ignition is a matter of dispute. Ball[10] showed that water loss from clay minerals can occur at low temperatures, most of water is lost between 450°C and 600°C. A linear regression between our loss on ignition results gives the following equations:

	$[r^2]$	[n]	
$[OM]_{600^\circ C} = 0.021 + 0.983\,[OM]_{450^\circ C}$	0.979	47	(7)

Equation 7 shows a slightly increase in the mass loss of samples due to the removal of most of the sorbed water at higher temperature. Therefore, a temperature of 600°C was used in carrying out the determination of the OM.

Figure 3 shows the relation between OM (estimated by loss on ignition method at 600°C) and TOC (dry combustion reference method). The following linear regression equation has been established:

	$[r^2]$	$[n]$	
$[OM]_{600^\circ C} = 6.03 + 1.956\,[TOC]$	0.44	47	(8)

This equation (8) suggests a stronger intercept effect. The intercept could result from the residual effect of inorganic components (such as hygroscopic and interlayer water) which were driven off by ignition at 600°C. This effect would be expected to be stronger in the study area which has slightly greater clay contents having high amount of water sorption capacity and large content of carbonate (%6.87) and sesquioxide. This intercept effect is in agreement of an earlier study by Grewal *et al.*[11].

As it was indicated before (equation 8), the regression analysis between OM and TOC gives a stronger intercept (6.03). In order to see the effect of clay content on the above mentioned relation, a further multiple regression between OM vs. TOC and clay content was made. The following relation is obtained:

	$[n]$	
$[OM]_{600^\circ C} = 3.39 + 1.763\,[TOC] + 0.1516\,[clay]$	47	(9)

Equation 9 suggests that the conversion factor is 1.763 (recovery factor 57%). This factor is very close to the conversion factor 1.72 in the earlier traditionally equation (OM = 1.72 TOC) published by Walkley and Black[4] and relatively close to the conversion factor (1.67) suggested by Grewal *et al.*[11]. Equations 8 and 9, indicate an intercept of 6.03

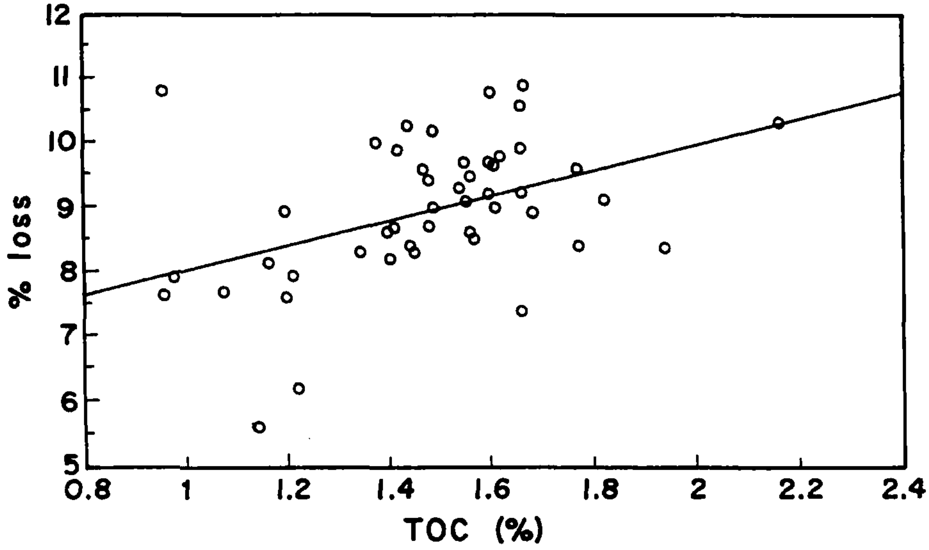

Figure 3 Linear regression between loss on ignition at 600°C (an estimator of organic matter, OM) and dry combustion (an estimator of total organic carbon, TOC).

and 3.39, respectively. This indicated that the inclusion of clay content has a positive effect on the obtained results in the study area. It is clear from these results, the factor of 1.72 is not valid where it simply assumes that the relationship between OM and TOC passes through the origin (a = 0). A more specific relation as in equation 9 should be applied for converting loss on ignition OM to total organic carbon TOC (specially for the Egyptian soil)

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