

# MEASUREMENT OF SOIL ORGANIC MATTER: A COMPROMISE BETWEEN EFFICACY AND ENVIRONMENTAL FRIENDLINESS

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## INTRODUCTION

The amount and type of organic matter influences soil moisture holding capacity, the storage and supply of exchangeable cations and other plant nutrients such as nitrogen and phosphorus, and the maintenance of stable soil structure and aeration. The organic matter fraction is very heterogeneous and includes plant, animal and microbial residues as well as stabilised products of decomposition generally termed humus. The types of compounds include carbohydrates such as simple sugars, fats, and oils as well as more complex polymers like hemicellulose, cellulose, lignin, waxes and resins. Nitrogen containing compounds include proteins, nucleic acids as well as individual amino acids and amines. It is difficult to measure the soil organic matter content due to this complexity.

Total organic matter is often estimated by loss on ignition (LOI) that involves measurement of the loss in weight when soils are ignited in a furnace. Depending on the conditions used, LOI methods can lead to errors due to release of bound water from inorganic constituents or evolution of carbon dioxide from carbonates. The measurement of organic carbon content gives an alternative way of estimating the organic matter content of the soil if an assumption is made about the average carbon content of the organic fraction. Organic carbon is normally measured by a dichromate oxidation such as that of Walkley and Black (1934) or by various wet or dry oxidation techniques that are followed by measurement of the carbon dioxide evolved. More information on the different methods available for estimating soil organic matter can be found in two recent reviews (Nelson and Sommers, 1996; Magdoff et al., 1996).

In this paper I compare a LOI procedure and a simple wet oxidation method with the standard Walkley-Black titration (WB-T) method that is currently used in our laboratory. The objectives were to determine if these alternative methods could produce accurate results with soils of low organic matter content, handle large numbers of samples and minimise our production of chemical waste. The trial used soils from a performance testing program operated by the Agricultural Laboratory Association of Southern Africa (ALASA). The results were analysed statistically and compared with the ALASA data set that had been generated over a three-year period by between 7 and 12 laboratories using the standard WB-T method.

## MATERIALS AND METHODS

A total of 67 soils were selected from those received for analysis in the ALASA testing scheme between January 1995

and December 1997. The laboratory had started using the WB-T method in late 1995 and up to the end of 1997 some 27 ALASA samples had been analysed. An additional 14 were analysed by this method in this study. All 67 soils were analysed by LOI and Walkley-Black Colourimetric (WB-C) methods.

### 1. WB-T method (Nelson and Sommers, 1982)

Soil organic matter is hydrolysed by an excess of a mixture containing sulphuric acid and potassium dichromate. The amount of unused potassium dichromate is determined by titration with ferrous sulphate using a diphenylamine indicator to detect the first appearance of unoxidised ferrous iron. Phosphoric acid is added to form a complex with ferric iron and provide a sharper colour change at the end point. Soil is air-dried and ground to < 2mm and a sample of between 0.25 and 5.0 g (sufficient to use between 35 and 75% of the dichromate) is added to a 500 ml Erlenmeyer flask. Then 10ml of 1 N (6 M) potassium dichromate solution is added, followed by 20 ml of concentrated sulphuric acid. The contents are mixed and the flask allowed to stand on a cork pad for 30 minutes. Then 200 ml of de-ionised water is added and the flask allowed to cool. Extra flasks are prepared without soil to standardise the ferrous sulphate and provide blank values. Before titration 10 ml of concentrated orthophosphoric acid and 0.5 ml of 0.16% barium diphenylamine sulphonate indicator solution are added. Titration is carried out by rapidly adding 0.5 N (0.5 M) ferrous sulphate solution until the colour of the soil digest changes to purple or blue then titrant is added drop by drop until the colour flashes to green and eventually to a light green end point. The blank flasks are titrated in the same way. It is assumed that only 77% of the organic matter is oxidised and a factor of 100/77 or 1.33 is used in the following calculation:

$$\% C = N \times \frac{V_1 - V_2}{S} \times 0.39$$

where:

- N = normality of ferrous sulphate solution
- V = ferrous sulphate solution used for blank (ml).
- V<sup>1</sup> = ferrous sulphate solution used for sample (ml)
- S<sup>2</sup> = weight of air-dry sample (g)
- 0.39 = 3 x 10<sup>3</sup> x 100 % x 1.33 (3 is the equivalent weight of carbon).

An empirical factor of 1.724 is used to convert organic carbon into organic matter:

$$\text{Organic matter (\%)} = \text{Organic carbon (\%)} \times 1.724$$

## 2. WB-C method (Rowell and Florence, 1993)

The oxidation reaction is similar to that above but the method differs in that the amount of reduced chromium is estimated colourimetrically (Sims and Haby, 1971) using a modification of the high volume version described by DeBolt (1974). Calibration is carried out using a solution of glucose (10 mg/ml) which is added to test tubes and dried overnight at 80°C. Between 50 and 500 mg of soil is weighed into tubes and 1 ml of 1 N (6 M) potassium dichromate is added, followed by 2 ml of concentrated sulphuric acid. The tubes are capped and heated in an oven at 80°C for 60 minutes. After the tubes have cooled the contents are diluted with 7 ml of de-ionised water, shaken and stood overnight in a refrigerator to allow the soil particles to settle. The absorbance of the supernatant is measured at 600 nm and the results related to the glucose calibration curve. A linear response occurs up to about 2.8 mg-C. Organic-C is converted into soil organic matter using the same factor as in the WB-T method.

## 3. LOI method (Schulte et al., 1991)

Combustion of soil at high temperature burns off the organic matter and leaves behind a mineral ash. At a temperatures in the 360 to 430 °C range errors due to decomposition of carbonates and release of structural water are minimised (Ball, 1964; Davies, 1974).

Air-dried soil (5 to 10 g) ground to < 2mm is weighed into weighed porcelain crucibles and dried at 105 °C. After reweighing to determine the oven dry weight, the crucibles are placed in a muffle furnace, the temperature is slowly raised to 360 °C and then the crucibles are heated for an additional 4 hours. The crucibles are allowed to cool in a desiccator and reweighed. The loss in weight between 105 °C and 360 °C gives an approximation of the total soil organic matter content.

$$\% \text{ Organic Matter (OM)} = \frac{[W_{105} - W_{360}]}{W_{105}} \times 100$$

where:

W<sub>105</sub> = weight of soil at 105 °C

W<sub>360</sub> = weight of soil at 360 °C

## 4. Data analysis

Managers of the ALASA program pool the data and determine the mean, the standard deviation and provide each participant laboratory with a z-score and rating for the 2 soils analysed each month. The z-score returns a positive or negative value relative to the deviation of the result from the mean in terms of the standard deviation. The z-score (z) is calculated from:

$$z = (x_i - m)/s$$

where:

x<sub>i</sub> is the result from laboratory i

m is the mean

s is the standard deviation.

It is assumed in this study that the ALASA mean and standard deviation reflects the true organic-C content and likely variability as measured by the WB-T method.

I also calculated the coefficient of variation (CV) for the ALASA data, which gives a comparison of variability between laboratories for results of varying magnitude. The CV is calculated from:

$$CV (\%) = s/m \times 100$$

Separate CVs were determined for between-run and within-run duplicate measurements in our laboratory using LOI and WB-C methods. Within-run comparisons were also made for the 27 duplicate soil results submitted to ALASA for the WB-T method. Between-run variability was not assessed for the WB-T method. Data sets for each method were visually compared by scatter plots and statistically analysed for correlation to produce linear regression equations. Performance was further assessed by comparing deviation and bias about the ALASA mean by examining individual z-scores and defining a mean z-score. It should be realised that the latter is not a true statistic when comparing data that has not contributed to calculation of the ALASA mean using the WB-T method.

## RESULTS AND DISCUSSION

Figures 1 to 3 show scatter plots and regression lines for correlation between the results from the 3 methods. Table 1 shows the regression equations generated. All results from our laboratory were highly significantly correlated with the ALASA data using the WB-T method. The LOI method gave the poorest and the WB-C the best correlation.

Inter-laboratory variability in the ALASA scheme was quite high, yielding a CV of about 20% (Table 2). Within-run and between-run variability using the three different methods at our laboratory was much lower and produced CV in the 3 to 7 % range.

The overall performance of each method in terms of accuracy and bias was assessed by comparing the deviation of each result from the ALASA WB-T mean and standard deviation (Table 3). This summary involved calculating a "mean z-score" as outlined in the table. The data suggests that the poor

Table 1. Correlation between three methods for organic carbon and organic matter

X	Y	n	Regression Equation	r <sup>2</sup>
Org-C %, WB-T [ALASA]	Org-C %, WB-T [lab]	41	Y = 0.9791(X) + 0.0282	0.89
Org-C %, WB-T [ALASA]	Org-C %, WB-C [lab]	67	Y = 0.9309 (X) - 0.0135	0.96
Org-C %, WB-T [ALASA]	OM %, LOI [lab]	67	Y = 2.1363 (X) + 0.2914	0.86

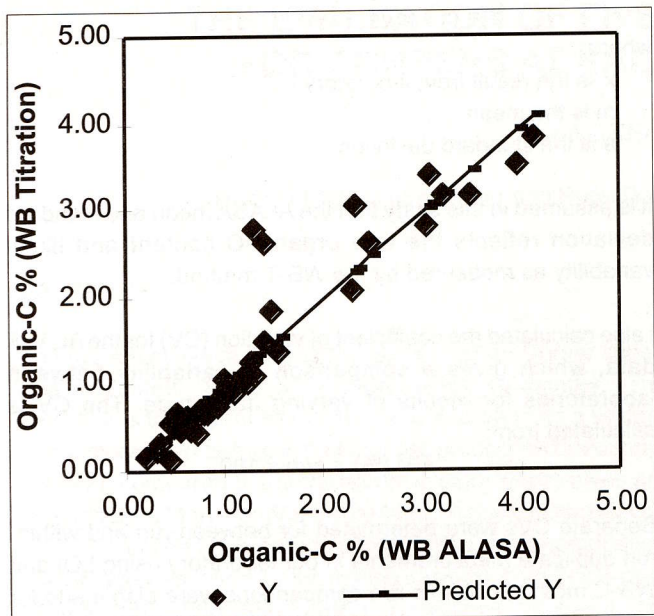


Figure 1. Comparison of the Walkley-Black titration method results from our laboratory with data from the ALASA performance testing scheme using the same method.

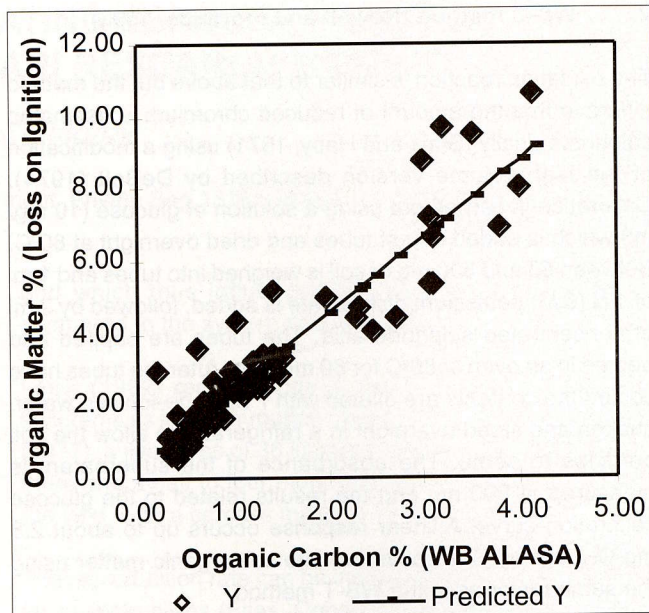


Figure 3. Comparison of Walkley-Black titration method results from the ALASA performance testing scheme with the results using a loss on ignition method at our laboratory.

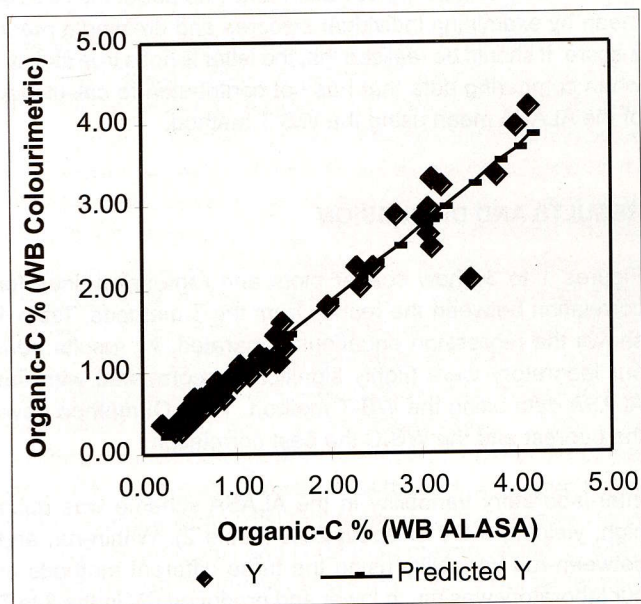


Figure 2. Comparison of Walkley-Black titration method results from the ALASA performance testing scheme with the colourimetric modification at our laboratory.

performance rating for the LOI method is in part due to the factor of 1.724 used to convert organic carbon to organic matter. If a factor of 2.2 is used, the positive bias in results is eliminated and the performance rating as determined from the mean z-score changes from a poor D-rating to a satisfactory B-rating. However, the LOI method is still inferior to the WB-C method. Despite good overall performance, both Walkley-Black methods gave results that were consistently lower than the ALASA mean. With the WB-C method this slight negative bias may be due to the nature of the calibration procedure. The WB-T method assumes that only 77% of the soil organic-C is oxidised while in the WB-C method it is assumed to be the same as glucose, an easily oxidisable compound.

Table 2. Comparison of variability in different methods tested

Method	Conditions tested	n	Mean CV (%)
WB-T	Variability between laboratories in ALASA scheme	67	19.9
WB-T	Within-run variability of our samples in ALASA scheme	23	4.7
WB-C	Within-run variability of duplicate measurements	67	5.3
WB-C	Between-run variability of duplicate measurements	67	6.8
LOI	Within-run variability of duplicate measurements	67	3.3
LOI	Between-run variability of duplicate measurements	67	5.3

Table 3. Performance rating using ALASA data

Method	n	Mean z-score <sup>3</sup>	Performance rating	% of results higher than ALASA mean
LOI (% C = % OM/1.724)	67	3.14	D	94.0
LOI (%C = %OM/2.2)	67	1.63	B	51.2
WB-T <sup>1</sup>	23	1.66	B	21.7
WB-T <sup>2</sup>	41	1.20	B	29.3
WB-C	67	0.69	A	23.9

<sup>1</sup>Samples actually submitted to the ALASA performance testing scheme

<sup>2</sup>Includes additional samples analysed later and not included in the ALASA performance testing scheme

<sup>3</sup>The mean z-score is determined by averaging all z-scores after they have been converted into positive scores

## CONCLUSIONS

Reliable results were obtained using the Walkley-Black titration method for organic carbon through the ALASA performance testing program. Equipment availability and technical time limits analysis to about 25 samples per day. For 1000 samples about 25 litres of concentrated sulphuric acid and over 500 g of potassium dichromate are consumed with a large proportion of chromium being discharged unchanged in the potentially hazardous hexavalent form. The colourimetric modification is more accurate, can handle 100 samples per day with less technical time and only 10% of the amount of chemicals. The LOI procedure uses no chemicals, can handle 45 samples in each batch but suffers from greater variability when compared to the organic carbon methods tested. All three procedures may be criticised in terms of intrinsic errors and the empirical nature of some calibration techniques.

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