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## Direct measurement of organic carbon content in soils by the Leco CR-12 carbon analyzer

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## **Direct Measurement of Organic Carbon Content in Soils by the Leco CR-12 Carbon Analyzer**

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### **ABSTRACT**

A straightforward procedure is described for soil organic carbon (C) measurement in soil samples that may contain carbonates by using the Leco CR-12 Carbon Analyzer. At a temperature of 840°C, a measured oxygen flow of 3.6 L min<sup>-1</sup>, lancing flow of 1.0 L min<sup>-1</sup>, soil organic C content can be directly measured on 0.20 to 0.40 g of samples, which have previously been ground to pass 40-mesh sieve, for most medium- and fine-textured soils. The organic C is combusted and measured within 2 min. A larger sample size of up to 2.5 g is suggested for sandy soils of low organic C content.

### **INTRODUCTION**

Early organic carbon measurements, either by dry combustion (Browning, 1938; Schollenberger, 1945) or by wet combustion (Walkley and Black, 1934; Allison, 1960) were not only labor intensive and time consuming, but not always accurate. The C recoveries with the methods varied from 63% to 87%, and the factors used for calibration ranged from 1.15 to 1.47 (Allison, 1960), which are related to the analysts' skill. The Leco CR-12 Carbon Analyzer (CR-12) for C determination is

capable of complete recovery and high precision, and is recommended primarily for total C analysis of soils and minerals. The system employs an infrared cell to measure the carbon dioxide ( $\text{CO}_2$ ) released upon combustion of the sample. The  $\text{CO}_2$  absorbs the IR energy at a specific wavelength and the reduction of IR energy is related to the  $\text{CO}_2$  level in the cell. The C content of the sample is determined by the total amount of  $\text{CO}_2$  produced by the combustion. Krom and Berner (1983) developed a method using the CR-12 to measure organic C content of geological samples that involved combustion of two subsamples at  $1350^\circ\text{C}$ , one of the subsamples had been pretreated by heating in a muffle furnace overnight at  $450^\circ\text{C}$  to oxidize organic C. The organic C content was derived from the difference between the two subsamples. Recently, Rabenhorst (1988) proposed a two-stage combustion method for soil organic C and carbonate C analysis. Chichester and Chaison (1992) adapted the procedure for use with the CR-12. For organic C measurements, instrument furnace temperature was set to  $575^\circ\text{C}$  and integration time was manually programmed for a minimum of 250 seconds to ensure complete recovery of  $\text{CO}_2$  from sample combustion. The samples previously combusted at low temperature were run a second time for inorganic C analysis by setting the furnace temperature at  $1000^\circ\text{C}$ , with an integration time of 250 seconds. Obviously, the procedures of the carbon analysis consume time and special caution is also needed in the process of the analysis because each sample has to undergo a second analysis. The objective of this experiment is to find specific conditions that can use the CR-12 to measure soil organic C directly.

### PRINCIPLES

Organic C can be oxidized completely at  $420^\circ\text{C}$  for a period of 45 min, whereas soil carbonates (calcite and dolomite) can be totally decomposed at  $850^\circ\text{C}$  for 30 min (Atkinson et al., 1958). Differential thermal analysis minerals indicate the decomposition of calcite begins at  $850^\circ\text{C}$ , reaches a peak at  $990^\circ\text{C}$  and ends rapidly at  $1005^\circ\text{C}$ . The thermal decomposition of dolomite has two individual peaks, one between  $750$  and  $830^\circ\text{C}$ , the other starting at  $850^\circ\text{C}$  and ending at  $980^\circ\text{C}$  (Beck, 1950). The marked difference between the temperature maximum at which organic C is completely combusted, and the minimum at which carbonates start to decompose provides the basis for the differentiation of organic C and inorganic carbonate by the CR-12. Theoretically, any temperature within the gap can be used for organic C analysis. Practically, higher temperature for organic C measurement are preferred, provided that carbonates in the samples are not decomposed.

### MATERIALS AND METHODS

Three sets of samples were used in this experiment: (i) mixtures of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) and calcium carbonate ( $\text{CaCO}_3$ ), both calibration standards; (ii) mixtures of two soil samples with different organic C and inorganic C contents

prepared by mixing finely ground Ah horizon soil (82.5 g kg<sup>-1</sup> organic C, 1.0 g kg<sup>-1</sup> inorganic C) with Cca horizon (3.0 g kg<sup>-1</sup> organic C and 44.7 g kg<sup>-1</sup> inorganic C); and (iii) soil samples from Saskatchewan in which the organic C content was previously measured by an accepted method. This set of samples was used to evaluate the precision of the proposed procedures. The measurement of organic C employed the following conditions: (a) the furnace temperature setting at 840°C; (b) measured oxygen flow of 3.6 L min<sup>-1</sup>; (c) lancing oxygen flow of 1.0 L min<sup>-1</sup>. Under the above conditions soil organic C content of 0.2 to 0.4 g of soil samples can be completely oxidized within 2 min.

## RESULTS AND DISCUSSION

### Differentiation of Organic and Inorganic Carbons by Leco CR-12 Carbon Analyzer

Evaluations over a range of combustion temperatures for organic and inorganic C indicated that organic C can not be completely recovered by the CR-12 at temperatures below 700°C. Temperatures above 700°C are necessary for the organic C to be completely combusted, keeping the CO<sub>2</sub> flow in the cell within the range where the detector works efficiently. If the CO<sub>2</sub> flow in the cell is lower than the sensitive level, the instrumental analytical process stops automatically, resulting in incomplete recovery of organic C at temperatures under 700°C, although it has been reported that a longer combustion time permits organic C to be completely oxidized even at lower temperature (Chichester and Chaison, 1992). As temperature increases, the time for organic C digestion decreases. When the furnace temperatures are set at 810°C to 840°C, organic C can be continuously and completely digested in a relatively short period of time. The actual time for organic C measurement, however, varies with the sample size. Carbonate minerals begin to decompose after 150 seconds in the furnace at a temperature of 840°C. The sample size needs to be adjusted in order to oxidize organic C completely while not breaking down carbonate C.

### Measurement of Organic Carbon Content on Defined Mixtures of Carbon Standards

Mixtures of sucrose (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) and calcium carbonate (CaCO<sub>3</sub>) were analyzed for organic C content. Sample size ranged from 0.25 to 0.45 g. After organic C analysis, the residues were analyzed a second time by setting the furnace temperature at 1100°C, to evaluate inorganic C recovery. All the organic C analyses of these samples were automatically ended within 120 seconds, prior to carbonate decomposition.

Organic C was determined with a high precision with all the standard deviation less than 5% (Table 1). The C contents of the reference samples were calculated from the weight of sucrose and calcium carbonate. Actual contents of the samples were a slightly different from the reference due to the losses in the process of

TABLE 1. Organic and inorganic C content determined by the CR-12 on mixtures of sucrose, calcium carbonate, and C-free soil.

Sample	Measured C content *			Calculated C content		
	Total	Organic (g kg <sup>-1</sup> )	Inorganic †	Total	Organic (g kg <sup>-1</sup> )	Inorganic
1	174.6±0.8	71.3±4.2	103.6±3.6	178.3	78.3	100.0
2	203.5±1.0	115.3±1.8	85.7±1.4	207.5	117.5	90.0
3	57.8±0.7	35.1±0.3	20.7±0.2	54.7	36.2	18.5
	n = 5	n = 5	n = 5			

\*Results are expressed as: mean ± standard deviation.

†Inorganic C was analyzed by running the sample a second time at 1100°C after organic C measurement.

TABLE 2. The C content of the simulated soil samples measured by the CR-12.

Sample	Calculated C content ‡		Measured C content *	
	Organic (g kg <sup>-1</sup> )	Inorganic	Organic	Inorganic † (g kg <sup>-1</sup> )
1	82.5	1.0	82.8 ± 1.1	0.8 ± 0.2
2	9.6	41.1	9.9 ± 0.7	42.8 ± 1.6
3	16.2	37.4	15.2 ± 1.4	36.8 ± 1.1
4	29.5	30.1	28.7 ± 2.1	31.7 ± 1.8
5	42.8	22.8	41.3 ± 1.8	24.5 ± 0.6
6	56.0	15.6	54.6 ± 1.3	15.1 ± 0.3
7	69.2	8.3	68.1 ± 1.0	8.9 ± 1.0
8	3.0	44.7	3.2 ± 0.2	48.0 ± 2.7
			n = 5	n = 5

‡The C contents were calculated based on the proportion of the Ah horizon and the Cca horizon, the total C measured on Leco CR-12 Carbon Analyzer and the inorganic C determined by the method of Tiessen et al. (1983).

\*Results are expressed as: mean ± standard deviation.

†Inorganic C was analyzed by running the sample a second time at 1100°C after organic C measurement.

sample preparation, as indicated by the total C contents measured. Inorganic C recovery from the sample residues was also within acceptable range. By using the above analytical procedure, both organic C and inorganic C can not only be separated but also recovered accurately by CR-12.

#### Measurement of Organic Carbon Content of Soil Mixtures

To further test the protocol based on standards, a set of simulated soil samples with different organic C and inorganic C contents were prepared by mixing finely ground Ah horizon soil (82.5 g kg<sup>-1</sup> organic C, 1.0 g kg<sup>-1</sup> inorganic C mainly as CaCO<sub>3</sub>) with a Cca horizon (3.0 g kg<sup>-1</sup> organic C and 44.7 g kg<sup>-1</sup> inorganic C) in different proportions, by which both organic and inorganic C contents can be calculated (Table 2). In preliminary analysis of organic C, we found that organic C oxidation overlapped with carbonate decomposition. This may, have resulted from oxidation of soil organic matter taking a longer time than sucrose or from the decomposition of the fine-grained calcite of the Cca horizon soil. Separation of organic C from carbonate-C can be done either by decreasing temperature to delay carbonate decomposition, or decreasing analysis time by reducing sample size. Soil carbonates start to decompose after 160 seconds of combustion at 810°C, as indicated by several runs. Decreasing temperature would further delay the organic C decomposition time and this would result in variable and unstable organic C values. Organic C can be completely digested within 120 seconds, with smaller samples, of 0.2 to 0.25 g. The C measurement by the CR-12 gives essentially the same values for organic C as determined indirectly by subtraction of inorganic C from total C by the traditional methods, even on soils that are high in both organic and inorganic C.

Recovery of the carbonate-C was evaluated by combusting the second time at 1100°C on the samples that have been analyzed for organic C. The slight differences between the carbonate-C and the inorganic C measured by the accepted method indicates that oxidation of organic C does not affect the recovery of carbonate C (Table 2).

It is stressed that sample size is a critical factor affecting the time needed for organic C oxidation, which, in turn, is closely related to the texture of the soils. For medium- and fine-textured soils, 0.20 to 0.40 g samples are suggested for organic C determination. For silty and sandy soils, the sample size can be increased to 0.4 to 1.0 g to obtain better representation. Good results were also obtained on 2.5 to 5.0 g of samples for sandy soils of low organic C content. The presence of dolomite may influence the accuracy for organic C measurement according to differential thermal analysis of the carbonate minerals (Beck, 1950). Dolomite will partially decomposed at temperature between 750 to 830°C which is lower than 840°C. However, it was not observed that organic C measurement was interrupted during the analytical process although those simulated soil samples had small amounts of dolomite, as indicated by X-ray diffraction analysis. Large amounts of dolomite in soil samples may result in an over estimation of organic C



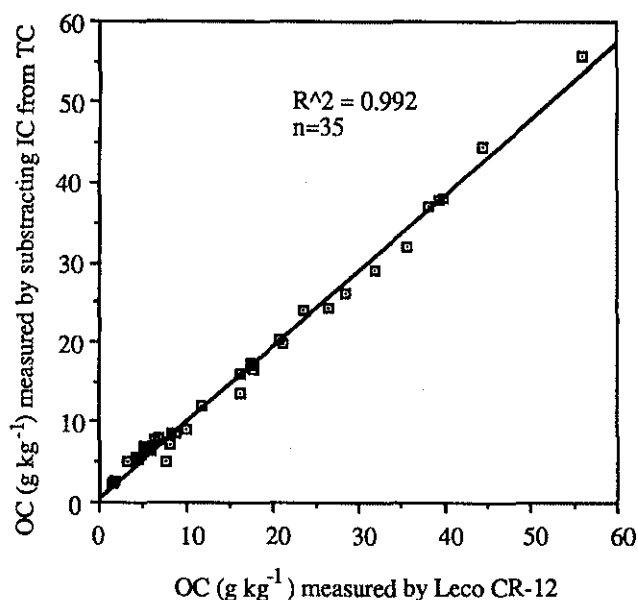


FIGURE 1. Comparison of soil organic C measurements by the CR-12 and the results of the subtraction of inorganic C (by Tiessen et al., 1983) from the total C (by the CR-12).

due to partial decomposition of the dolomite. Fortunately, in most soil samples, particularly A and B horizons, dolomite is not an important component.

#### Soil Sample Analyses

In order to evaluate the precision of the procedure, a set of soil samples from Saskatchewan with organic C contents of 1.0 to 56.0 g kg<sup>-1</sup> and carbonate-C contents of 0 to 32.5 g kg<sup>-1</sup> was selected for analysis. A comparison of soil organic C measurements by the CR-12 procedure and by the subtraction of inorganic C from total C (Tiessen et al., 1983) was made. Very high linear correlation between two methods over the range of 1.0 to 56.0 g kg<sup>-1</sup> indicates a wide validity of the procedure for soil organic C measurement (Figure 1). The CR-12 procedure eliminates labor intensive and time consuming processes, such as acid pretreatment (as suggested by Leco Company), removing organic C at 450 to 500°C overnight (Krom and Berner, 1983) and changing furnace temperature during combustion (Chichester and Chaison, 1992). This instrumental analysis also allows one to use automated computerized data acquisition techniques to increase efficiency. On average, these changes provide much faster organic C measurements, permitting an analyst to easily make up to 200 determinations per day.

The standard used for calibration of the instrument can be a real soil sample that has known organic C content. Sucrose that has been popularly used for calibration of the system would be suitable for the organic residues, but not suitable for mineral soils because of its extremely high organic C content. It should be pointed out that the time for organic C measurement by the Leco CR-12 Carbon Analyzer must be done with 130 seconds. Samples requiring a longer combustion period should be reduced in size, especially those with high inorganic C contents.

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