Total Organic Carbon (TOC) Determination: Comparing Two Different Approaches to Acid Treatment in Preparation for Combustion Analysis

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Introduction

Total Organic Carbon (TOC) in soil and rock is a common analysis used for determining locations of natural hydrocarbon fossil fuel deposits as well as an indicator for overall soil health. TOC determination is commonly performed indirectly by acid treatment of the sample to effervesce the carbon dioxide from the inorganic carbonate species. Several documented methods, including ISO 10694, recommend the use of hydrochloric acid for the removal of carbonates as it is strong enough to react with the carbonates, but does not react excessively with organic carbon. This method is sometimes referred to as Non-Carbonate Carbon Determination and is used to closely estimate TOC.

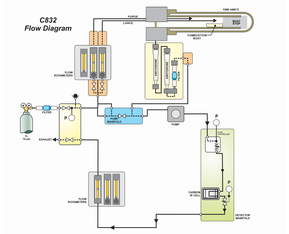
Total carbon combustion instruments use a high-temperature furnace to achieve complete decomposition of the sample. The organic carbon that remains following acid treatment is oxidized by the pure oxygen environment and converted to CO_2. The gas is swept through the instrument reagents and carried to the infrared detectors where the infrared absorbance of CO_2 is measured and converted to a quantifiable carbon concentration based on initial sample mass.

Data will be presented using two different sample preparation approaches for TOC determination. The first, more classical approach, uses a watch glass for acid treatment, followed by the transfer of the remaining sample to a ceramic combustion boat for analysis. The second approach uses a newly developed non-porous ceramic combustion boat, which allows for acid treatment to be performed directly in the boat prior to analysis, thereby eliminating the sample transfer step. Results from these two approaches will be compared for both hydrophilic and hydrophobic soil samples; including soil reference materials.

Published Method

ISO 10694: Soil Quality – Determination of Organic and Total Carbon after Dry Combustion (Elementary Analysis). Direct combustion after acid treatment is commonly performed using resistance and induction furnace analyzers.

C832



C832 Theory of Operation

The LECO C832 is a macro combustion carbon determinator that utilizes a pure oxygen environment in a high-temperature horizontal ceramic combustion furnace.

- A combustion boat containing a sample is transferred into the furnace (typically 1350 °C) with a pure oxygen environment to ensure complete combustion of the sample.
- The sample combusts, releasing carbon as CO_2 gas.
- Additional oxygen is introduced directly above the sample via a ceramic lance to accelerate the combustion of refractory materials.
- The combustion gases are swept to the back of the furnace then forward between the inner and outer furnace tubes, allowing the gases to remain in the high-temperature zone, ensuring efficient oxidation.
- The combustion gases then flow through a drying agent for moisture removal, and a flow controller regulates the flow as the gases are carried through the non-dispersive infrared detection (NDIR) cell for carbon detection (as CO_2).

Sample Preparation

For optimal precision, a representative, uniform sample is required. Samples should be ground to a fine powder.

Expressing carbon content on a dry basis is a crucial factor in reporting accurate carbon results. It is recommended that samples for total carbon determination either be dried in an oven for 1 hour at 105 °C prior to weighing and analysis, or a moisture content be determined on the day of analysis, which can be used for a dry basis correction of the carbon results using the instrument's software. It is recommended that samples for TOC determination be dried in an oven for 1 hour at 105 °C prior to weighing and subsequent acid treatment.

Separate portions of the sample material should be used for Total Carbon and TOC determination. Samples for TOC determination should be treated with dilute hydrochloric acid and dried in an oven to remove excess acid.

Hydrophilic Versus Hydrophobic Materials

Soil, rock, and related materials may have different water absorption properties due to the components of the material. Typically, materials that have low organic carbon contents are more likely to absorb or be miscible with aqueous acid treatments. These hydrophilic materials can be acid treated without any prior treatment with a surfactant to break the surface tension of the water. Alternatively, hydrophobic samples will have little-to-no interaction with the acid treatment process due to the repelling forces between the hydrophobic sample and the water carrying the acid. Hydrophobic soils and rock samples typically have a high organic carbon content with a nonpolar nature within the material. Therefore, hydrophobic materials will require pretreatment with a surfactant prior to acid treatment in order to ensure that the acid reacts with the carbonate carbon within the material. Refer to LECO Application Note "Determination of Total Organic Carbon in Soil, Rock, and Shale by Acid Digestion and Combustion" (LECO Form No. 203-821-679) for details regarding the preparation of the dilute surfactant.

Hydrophilic materials absorb aqueous solutions

Hydrophobic materials repel aqueous solutions

Acid Treatment Methods

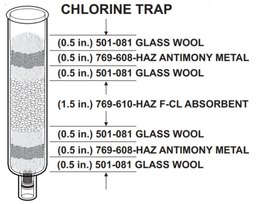
Watch Glass Method

1. Weigh dried sample onto a 2–3 inch Watch Glass. Record the mass.
   Note: Acid treatment cannot be performed directly in the standard 528-203 Ceramic Combustion Boats due to their porous nature.
2. Add ~1.0 mL of diluted surfactant solution to the sample, if necessary.
3. Add ~1.0 mL of 1:3 HCl:H2O (3N) solution to completely wet the sample.
4. Dry sample in oven at 105 °C for one hour, or until dry.
5. Repeat steps 2-4 until no more effervescence is observed.
6. Pre-bake LECO 528-203 Ceramic Combustion Boats at 1000 °C for 40 min. Allow to cool in a desiccator.
7. Scrape dried sample from the Watch Glass into a pre-baked 528-203 Ceramic Combustion Boat.
8. Analyze sample.

Non-Porous Combustion Boat Method

1. Pre-bake LECO 528-206 Non-Porous Ceramic Combustion Boats at 1000 °C for 40 min. Allow to cool in a desiccator.
2. Weigh dried sample onto a preheated 528-206 Non-Porous Ceramic Combustion Boat. Record the mass.
3. Add ~1.0 mL of diluted surfactant solution to the sample, if necessary.
4. Add ~1.0 mL of 1:3 HCl:H2O (3N) solution to completely wet the sample.
5. Dry sample in oven at 105 °C for one hour, or until dry.
6. Repeat steps 2-4 until no more effervescence is observed.
7. Analyze sample.

Note: When acid-treated samples are combusted, chlorine will be produced, which can damage the instrument. In order to minimize this damage, a halogen (chlorine) trap must be installed in the secondary reagent tube prior to analyzing any acid-treated samples. Refer to LECO Product Information Bulletin No. 202-001-315 Halogen Trap Kit Instructions and the diagram below.



Non-Porous Combustion Boats

The 528-206 Non-Porous Ceramic Combustion Boats may be reused for multiple analyses (typically 5 to 7 analyses), depending on the nature of the samples and if proper cleaning and handling is utilized; however, they should be visually inspected for any signs of damage or cracking prior to each reuse, and if any damage or cracking is observed, they should be discarded.

When using the Non-Porous Ceramic Combustion Boats with an autoloader, a sample cool time of 15 seconds should be used in the software method parameters (Cornerstone 3.1.X or greater), and a lining of ~60 g of 501-608 Quartz Wool should be added to the bottom of the boat bucket to cushion the impact of the boat when it drops into the bucket. Both practices will extend the boat's lifetime.

Sample Description

- LECO 502-694 Soil (13.61% ± 0.32% C)*
- LECO 502-697 Soil (3.05% ± 0.03% C)
- LECO 502-982 Soil (22.7% ± 0.3% C)*

**Soil samples were hydrophobic and therefore required pre-treatment with a dilute surfactant solution prior to acid treatment.*

Method Parameters

Parameter	Setting
Furnace Temperature	1350 °C
Lance On Delay	20 Seconds
Manual Loading Model	Single Sample
Nominal Mass	1.0000 g

Element Parameters

Parameter	Setting
Wait for Baseline Stability	Yes
Starting Baseline	2 Seconds
Use Comparator	Yes
Comparator Level	0.30 %
Minimum Integration Time	90 Seconds
Maximum Integration Time	360 Seconds
Auto Detect Data Missed Time	3 Seconds
Integration Delay	0 Seconds

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Sample Results

Data was generated utilizing a linear, full regression calibration using fractional masses (~0.1 g to ~0.25 g) of LECO 502-950 LCRM Synthetic Carbon (0.14% C), LECO 502-696 LCRM Synthetic Carbon (1.01% C), LECO 502-905 LCRM Synthetic Carbon (5.00% C) and fractional masses (~0.1 g to ~0.5 g) of LECO 502-902 LCRM Calcium Carbonate (12.03% C). The calibration was verified with LECO 502-696 LCRM Synthetic Carbon (1.01% C).

Sample	% Total Carbon	% Standard Deviation
LECO 502-694 Soil	13.83	0.07
LECO 502-697 Soil	3.07	0.01
LECO 502-982 Soil	22.8	0.05

	Watch Glass Method		Non-Porous Boat Method	
Sample	% TOC	% Std Dev	% TOC	% Std Dev
502-694 Soil	11.48	0.3	12.75	0.09
502-697 Soil	2.47	0.03	2.52	0.02
502-982 Soil	19.56	0.55	20.3	0.05

Observations

The results demonstrate enhanced TOC recovery for the Non-Porous Boat Method compared to the Watch Glass Method. The decrease in TOC recovery when using the Watch Glass Method is likely due to sample loss during sample transfer from the watch glass to the combustion boat. It is difficult to scrape all of the dried sample from the watch glass and some sample material will be left behind on the glass. Some sample material may also be spilled when transferring the sample to the boat.

The results show improved precision for the Non-Porous Boat Method compared to the Watch Glass Method. The poorer precision for the Watch Glass Method is likely due to varying degrees of sample loss between the different sample replicates.

The Non-Porous Boat Method allows for acid treatment to be performed directly in the combustion boat, eliminating the need for sample transfer and potential sample loss, therefore improving both recovery and precision.

Conclusions

There are many advantages to using the Non-Porous Combustion Boats. Among these advantages are:

- **Enhanced Recovery**
  Performing acid treatment directly in the combustion boat eliminates the need for sample transfer and potential sample loss.
- **Improved Precision**
  Eliminating the sample transfer step avoids varying degrees of sample loss between sample replicates.
- **Use with Automation**
  The Non-Porous Combustion Boats can be used with an autoloader, which increases sample throughput and ease-of-use.
- **Reusable Boats**
  The Non-Porous Combustion Boats are reusable for multiple analyses (typically 5 to 7 analyses), making them a cost-effective choice.
- **Ease-of-Use**
  Using the Non-Porous Combustion Boats eliminates the sample transfer step, simplifying the procedure. This eliminates the need for cleaning watch glasses as well.
- **Requires Less Drying Oven Space**
  The Non-Porous Combustion Boats take up less space in the drying oven compared to watch glasses, therefore increasing the number of samples that can be dried simultaneously.

References

- LECO Application Note: "Determination of Total Organic Carbon in Soil, Rock and Shale by Acid Digestion and Combustion" (LECO Form No. 203-821-679).
- ISO 10694: Soil Quality – Determination of Organic and Total Carbon after Dry Combustion (Elementary Analysis).