Application Note

Instrument: C832

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Determination of Total Organic Carbon in Soil, Rock, and Shale by Acid Digestion and Combustion

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Introduction

Total organic carbon (TOC) determination in soil, rock, and shale is a common analytical tool used for determining locations of natural hydrocarbon fossil fuel deposits. The organic carbon richness of rock samples (TOC%) is one of the most important parameters used in the evaluation of sediments as a potential source for petroleum or natural gas. TOC content controls the hydrocarbon generation ability of rock and the content of adsorbed natural gas within the rock, as it is the source material responsible for the formation of natural hydrocarbon fossil fuel deposits.

TOC determination can also be used for the assessment of soil quality in agriculture and as a quality control parameter for raw building materials. TOC content is one of the most important constituents of soil due to its capacity to affect plant growth as both a source of energy and a trigger for nutrient availability through mineralization. The determination of TOC is also an important quality control parameter used during the manufacturing of cement, from the raw material until the final product.

Instrument Model and Configuration

The LECO C832 is a macro combustion carbon determinator that utilizes a pure oxygen environment in a high-temperature horizontal ceramic combustion furnace designed to handle macro sample masses. A weighed sample is combusted, and the combustion gases are swept from the furnace and through anhydrone tubes for the removal of moisture. The combustion gases are then carried to a non-dispersive infrared (NDIR) cell for the detection of carbon (as CO_2).

Method Reference

ISO 10694: Soil Quality - Determination of Organic and Total Carbon after Dry Combustion (Elementary Analysis)

Method Summary

TOC determination is most commonly performed by acid treatment of the sample to effervesce the carbon dioxide from the inorganic carbonate species. This is often referred to as the acid digestion method. Several documented methods, including ISO 10694, recommend the use of dilute 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, leaving the TOC content intact. The acid-treated sample can then be analyzed to determine the TOC content. This method is sometimes referred to as the non-carbonate carbon method and is used to closely estimate TOC content.

A weighed sample is treated with dilute acid to remove carbonate carbon and then dried in an oven to remove excess acid. The dried acid-treated sample is then analyzed to determine the non-carbonate carbon content of the material, which is usually referred to as the total organic carbon (TOC) content. A separate portion of a non-acid-treated sample can be analyzed to determine the total carbon content of the material. Obtaining a total carbon value allows for the inorganic carbon (TIC) content of the material to be calculated by difference.

Sample Preparation

A representative, uniform sample is required. Samples should be ground to a fine powder. Samples should be dried prior to analysis or corrected for moisture (see note below). Samples for TOC determination should be treated with dilute acid following the procedure outlined in the Acid Treatment for TOC Determination procedure section in the TOC Determination portion of the Procedure. Separate portions of the sample material should be used for Total Carbon and TOC determination. Reference materials should be prepared according to the instructions on the certificate.

Note: 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 acid treatment.

Accessories

Total Carbon Determination

528-203 Ceramic Combustion Boats*, 761-929 Crucible Tongs, and 501-614 Spatula

Non-Carbonate (TOC) Determination

528-206 Non-Porous Ceramic Combustion Boats*, 202-001-315 Halogen Trap Kit, 502-889 LECONAL Concentrate (for use on hydrophobic samples, diluted as noted in the Procedure), a 1:3 HCl:H_2O (3N) solution, 761-929 Crucible Tongs, 501-614 Spatula, and a graduated pipette

**For optimal precision, combustion boats should be baked in a muffle furnace at 1,000°C for a minimum of 1 hour prior to use. Once the combustion boats have cooled, they should be transferred to a desiccator for storage until use. If the combustion boats are not used within twenty-four hours, they should be re-baked. After baking, handle combustion boats and liners with clean tongs only; do not use fingers.*

Note: The 528-206 Non-Porous Ceramic Combustion Boats are specifically designed so that acid treatment can be performed directly in the boat. These boats may be reused for multiple analyses; 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 an autoloader, LECO recommends lining the boat bucket with ~ 60.0 g of 501-608 Quartz Wool to cushion the impact of the boat when it drops in to the bucket in order to extend boat lifetime.

Reference Materials

LCRM®, LRM®, NIST, or other suitable reference materials.

Method Parameters

Furnace Temperature	1350 °C
Lance On Delay	20 s
Manual Loading Model	Single Sample
Nominal Mass	1.0000 g
Sample Cool Time	15 s (Autoloaders)

Element Parameters

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

Note: Refer to 832 Series Operator's Instruction Manual for Parameter definitions.

Procedure for Total Carbon Determination

1. Prepare instrument for operation as outlined in the operator's instruction manual.
2. Condition the System.
   a. Select three or more sample replicates in the Login screen.
   b. Weigh ~0.25 g of calcium carbonate (or soil sample) into a pre-baked 528-203 Ceramic Combustion Boat.
   c. Enter sample mass and identification into the Login screen.
   d. Place the ceramic combustion boat containing the sample in front of the furnace entrance (for manual loading systems), or into the appropriate position in the autoloader.
   e. For manual loading systems, initiate the analysis sequence, and when prompted by the software, load the ceramic combustion boat containing the sample into the furnace and press the Analyze button.
   f. Perform steps 2b through 2d (or 2b through 2e for manual loading systems) a minimum of three times.
   g. For autoloading systems, initiate the analysis sequence.
3. Determine Instrument Blank.
   a. Select five or more blank replicates in the Login screen.
   b. Place a pre-baked 528-203 Ceramic Combustion Boat in front of the furnace entrance (for manual loading systems) or place the required number of pre-baked ceramic combustion boats (minimum of five) into the appropriate positions in the autoloader.
   c. For manual loading systems, initiate the analysis sequence, and when prompted by the software, load the ceramic combustion boat into the furnace and press the Analyze button.
   d. For manual loading systems, perform steps 3b through 3c a minimum of five times.
   e. For autoloading systems, initiate the analysis sequence.
   f. Set the blank following the procedure outlined in the operator's instruction manual.

   Note: The standard deviation of the last three blanks should be less than or equal to 0.001% (10 ppm). Additional blanks beyond the recommended five may be required in order to achieve the recommended precision.
4. Calibrate/Drift Correct.
   a. Select the desired number of calibration/drift replicates in the Login screen (minimum of five).
   b. Weigh an appropriate mass of a suitable reference material into a pre-baked 528-203 Ceramic Combustion Boat and spread the material evenly within the combustion boat.
   c. Enter sample mass and identification into the Login screen.
   d. Place the ceramic combustion boat containing the reference material in front of the furnace entrance (for manual loading systems), or into the appropriate position in the autoloader.

e. For manual loading systems, initiate the analysis sequence, and when prompted by the software, load the ceramic combustion boat containing the sample into the furnace and press the Analyze button.
f. Perform steps 4b through 4d (or 4b through 4e for manual loading systems) a minimum of three times for each calibration/drift sample used.
g. For autoloading systems, initiate the analysis sequence.
h. Calibrate or drift correct the instrument following the procedure outlined in the operator's instruction manual.
i. Verify the calibration/drift correction by analyzing an appropriate mass of another/different suitable reference material, following steps 4b through 4g, and confirm that the results are within the acceptable tolerance range.

5. Analyze Samples.
   a. Select the desired number of sample replicates in the Login screen.
   b. Weigh ~0.25 g to ~0.5 g of the sample into a pre-baked 528-203 Ceramic Combustion Boat and spread the sample evenly within the combustion boat.
   c. Enter sample mass and identification into the Login screen.
   d. Place the ceramic combustion boat containing the sample in front of the furnace entrance (for manual loading systems), or into the appropriate position in the autoloader.
   e. For manual loading systems, initiate the analysis sequence, and when prompted by the software, load the ceramic combustion boat containing the sample into the furnace and press the Analyze button.
   f. Perform steps 5b through 5d (or 5b through 5e for manual loading systems) for each sample to be analyzed.
   g. For autoloading systems, initiate the analysis sequence.

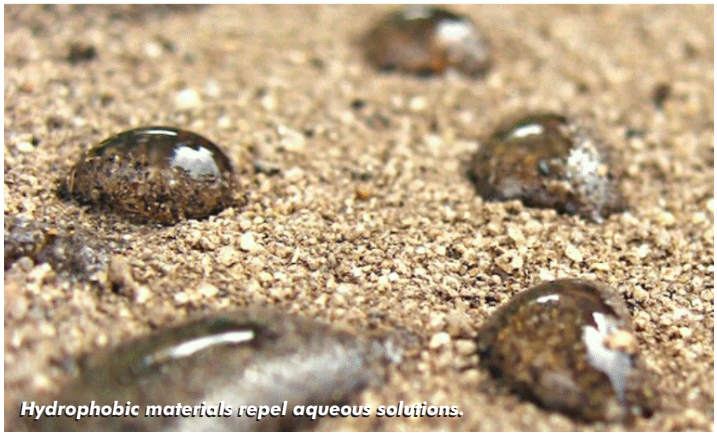
Procedure for TOC (Non-Carbonate Carbon) Determination

Acid Treatment for TOC Determination (Sample Preparation for TOC)

1. Weigh ~0.25 g to ~0.5 g of the dried sample into a pre-baked 528-206 Non-Porous Ceramic Combustion Boat and spread the sample evenly within the combustion boat. Record the mass (This is the mass that will be entered into the instrument Login screen for analysis of the sample following acid treatment).
2. Using a graduated pipette, add ~1.0 mL of 1:3 HCl:H_2O (3N) solution to completely wet the sample. The sample will effervesce, indicating a reaction between the HCl solution and the carbonates within the sample. If the HCl solution beads on the surface of the sample rather than soaking in, refer to the Note below.
3. Dry the acid treated sample in the combustion boat in a drying oven (~105 °C) for one hour, or until dry.
4. Perform Steps 2 through 3 until no additional effervescing occurs (typically three or more treatments are required).

Note: Some material will be hydrophilic and will readily absorb the HCl solution, while some material may be hydrophobic, and will repel the HCl solution, preventing it from soaking into the sample. If the acid solution beads on the sample rather than soaking in, the sample is hydrophobic (see images below). It is important that the acid solution soaks into the material so that it can react with the carbonate carbon within the sample. To allow for the absorption of the acid solution into hydrophobic materials, a surfactant is added to the sample prior to acid treatment. The procedure below should be used to make a surfactant solution, if needed. Add ~0.1 mL of the surfactant solution to the hydrophobic samples before acid treating the samples and acid blank samples. Do not add additional surfactant solution during subsequent acid addition steps. If a material is hydrophobic and requires treatment with a surfactant solution, the acid blank samples should be pre-treated with surfactant solution as well, prior to acid treatment.


Hydrophilic materials absorb aqueous solutions.


Hydrophobic materials repel aqueous solutions.

Procedure for preparing Surfactant Solution for treatment of Hydrophobic Samples

1. Using a graduated pipette, add 0.1 mL of LECO 502-889 LECONAL™ concentrate to a clean 100 mL volumetric flask and dilute to volume using deionized water. Mix thoroughly.
2. Using a fresh graduated pipette, add 1.2 mL of the prepared dilute LECONAL solution to a separate clean 100 mL volumetric flask and dilute to volume using deionized water. Mix thoroughly prior to use.

Sample Preparation for Acid Blank Determination and Carbonate Removal Verification

1. Prepare Samples for Acid Blank Determination.
   a. Using a pipette, weigh ~1.0 mL of 1:3 HCl:H_2O (3N) solution into a pre-baked 528-206 Non-Porous Ceramic Combustion Boat.
   b. Dry the acid blank sample in the combustion boat in a drying oven (~105 °C) for one hour, or until dry.
   c. Perform steps 1a through 1b the same number of times as the samples were treated.

   Note: If a surfactant was used for hydrophobic soil samples, the same volume of surfactant solution should be added to the combustion boat along with the acid solution for acid blank determination.

2. Prepare samples for Carbonate Removal Verification.

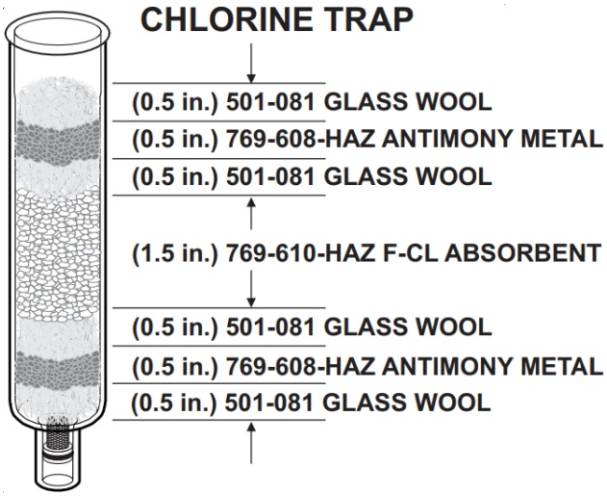
   Note: Acid-treated calcium carbonate (or synthetic carbon) samples are analyzed in order to verify that the acid treatment procedure was successful in removing carbonate carbon. Results for the acid-treated calcium carbonate (or synthetic carbon) samples should be <0.1% C to confirm successful removal of carbonates. The same amount of acid solution and number of treatments must be used to treat the samples, calcium carbonate samples, and acid blank samples.

   a. Weigh an equivalent mass** of calcium carbonate, or synthetic carbon into a pre-baked 528-206 Non-Porous Ceramic Combustion Boat and spread the sample evenly in the combustion boat. Record the mass (This is the mass that will be entered into the instrument Login Screen for analysis of the sample following acid treatment).
   b. Treat the sample with the equivalent volume of HCl solution that was used to treat the samples. When samples containing high amounts of carbonates are treated, heavy effervescence will occur. Therefore, it is recommended that the acid solution be added slowly to the sample to prevent sample loss.
   c. Dry the acid treated calcium carbonate (or synthetic carbon) sample in the combustion boat in a drying oven (at ~105 °C) for one hour, or until dry.
   d. Perform steps 2b through 2c the same number of times as the samples were treated.

   ***For optimal precision, the mass of calcium carbonate (or synthetic carbon) used to verify carbonate removal should be the same mass as the samples being analyzed.*

Analysis Procedure for TOC Determination

1. Prepare instrument for operation as outlined in the operator's instruction manual.
2. Install a Halogen (Chlorine) Trap on the instrument in the secondary reagent tube (refer to LECO Product Information Bulletin No. 202-001-315 Halogen Trap Kit Instructions, and the diagram below).



3. Condition the system.
   a. Follow the same procedure for conditioning the system as outlined in step 2 of the Total Carbon Determination section of the procedure.

   Note: Fresh chlorine trap reagents may require conditioning by analyzing one to two acid treated samples or a material containing an equivalent mass percent of chlorine. The trap has been depleted when the F-Cl Absorbent has turned a dark brown color and/or the bottom layer of the antimony metal has become tarnished.

4. Determine Instrument Blank.†
   a. Follow the same procedure for determining the instrument blank as outlined in step 3 of the Total Carbon Determination section of the procedure.

   Note: For optimal precision, pre-baked 528-206 Non-Porous Ceramic Combustion Boats should be used when determining the instrument blank for TOC determination.

   †Instrument blanks are used to set the blank for the reference materials, and acid blanks are used to set the blank for the acid-treated samples.

5. Determine Acid Blank.†
   a. Select three or more blank replicates in the Login screen.
   b. Place a 528-206 Non-Porous Ceramic Combustion Boat containing a dried acid sample (prepared in step 1 of the Sample Preparation for Acid Blank Determination procedure) in front of the furnace entrance (for manual loading systems) or place the required number of combustion boats containing dried acid samples into the appropriate positions in the autoloader.
   c. Enter the appropriate sample identification information into the appropriate fields in the Login screen.
   d. For manual loading systems, initiate the analysis sequence, and when prompted by the software, load the combustion boat into the furnace and press the Analyze button.
   e. For manual loading systems, perform steps 5b through 5d a minimum of three times.
   f. For autoloading systems, initiate the analysis sequence.
   g. Set the acid blank following the blank procedure outlined in the operator's instruction manual.

   †Instrument blanks are used to set the blank for the reference materials, and acid blanks are used to set the blank for the acid treated samples.

6. Calibrate/Drift Correct.
   a. Follow the same procedure for calibrating the Instrument as outlined in step 4 of the Total Carbon Determination section of the procedure.

   Note: For optimal precision, pre-baked 528-206 Non-Porous Ceramic Combustion Boats should be used when calibrating the instrument for TOC determination.

7. Analyze Acid-Treated Calcium Carbonate (or Synthetic Carbon) Samples for Verification of Carbonate Removal.
   a. Select the desired number (minimum of three) of carbonate removal verification replicates in the Login screen.
   b. Place a 528-206 Non-Porous Ceramic Combustion Boat containing an acid treated calcium carbonate (or synthetic carbon) sample (prepared in step 2 of the Sample Preparation for Carbonate Removal Verification procedure) in front of the furnace entrance (for manual loading systems) or place the required number of combustion boats containing acid-treated calcium carbonate samples into the appropriate positions in the autoloader.
   c. Enter the recorded mass of the untreated sample (mass of the sample prior to the acid treatment procedure) and the sample identification information into the appropriate fields in the Login screen.
   d. For manual loading systems, initiate the analysis sequence, and when prompted by the software, load the ceramic combustion boat containing the sample into the furnace and press the Analyze button.
   e. For manual loading systems, perform steps 7b through 7d for each sample to be analyzed.
   f. For autoloading systems, initiate the analysis sequence.

   Note: Results for the acid-treated calcium carbonate (or synthetic carbon) samples should be < 0.1% C to confirm successful removal of carbonates.

8. Analyze Samples.
   a. Select the desired number of sample replicates in the Login screen.
   b. Place a 528-206 Non-Porous Ceramic Combustion Boat containing an acid-treated sample (prepared in the Acid Treatment for TOC Determination section of the procedure) in front of the furnace entrance (for manual loading systems) or place the required number of combustion boats containing acid-treated samples into the appropriate positions in the autoloader.
   c. Enter recorded mass of the dried, untreated sample(s) (mass of sample after drying and prior to the acid treatment procedure) and the sample identification information into the appropriate fields in the Login screen.
   d. For manual loading systems, initiate the analysis sequence, and when prompted by the software, load the ceramic combustion boat containing the sample into the furnace and press the Analyze button.
   e. For manual loading systems, perform steps 8b through 8d for each sample to be analyzed.
   f. For autoloading systems, initiate the analysis sequence.

Typical 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	*Mass (g)*	*% Total Carbon*	*Mass (g)*	*% TOC*
Soil	0.2562	13.82	0.2498	12.65
LECO 502-694	0.2534	13.95	0.2568	12.67
13.61% ± 0.32% C	0.2481	13.79	0.2465	12.83
	0.2483	13.81	0.2457	12.74
	0.2487	13.77	0.2483	12.85
	Avg =	***13.83***	***Avg =***	***12.75***
	s =	***0.07***	***s =***	***0.09***
Soil	0.2477	3.07	0.2506	2.50
LECO 502-697	0.2515	3.06	0.2510	2.54
3.05% ± 0.03% C	0.2543	3.09	0.2488	2.53
	0.2542	3.06	0.2499	2.51
	0.2543	3.06	0.2529	2.53
	Avg =	***3.07***	***Avg =***	***2.52***
	s =	***0.01***	***s =***	***0.02***
Soil	0.2499	22.9	0.2480	20.3
LECO 502-982	0.2481	22.8	0.2492	20.3
22.7% ± 0.3% C	0.2474	22.8	0.2542	20.3
	0.2477	22.8	0.2434	20.3
	0.2517	22.7	0.2525	20.2
	Avg =	***22.8***	***Avg =***	***20.3***
	s =	***< 0.1***	***s =***	***< 0.1***

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