Total Organic Carbon (TOC) Analysis of Soil and Rock Comparing Various Elemental Analysis Techniques

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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. TOC determination is most 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 and is used to closely estimate TOC. Direct measurement of TOC is difficult due to the unique properties of soil and rock, and must be performed using a temperature-dependent differentiation method.

Total carbon combustion instruments use either a high-temperature resistance furnace or a high-temperature induction furnace to achieve complete decomposition of the sample. The carbon 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 concentration based on initial sample mass.

This poster presentation will cover the comparison of TOC determination on various total carbon analysis techniques with or without the use of acid treatment to remove the inorganic carbon species. This comparison will include samples that are hydrophilic and hydrophobic to the acid treatment process. Data will be examined that includes soil reference materials and rock samples.

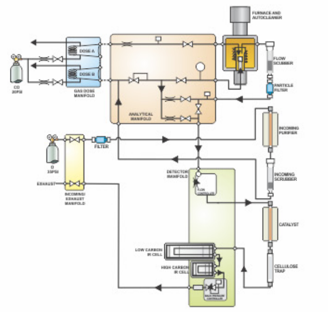
Published Methods

- DIN 19539: Investigation of Solids – Temperature-Dependent Differentiation of Total Carbon (TOC400, ROC, TIC900). This method utilizes temperature differentiation combined with oxidative and non-oxidative carrier gases.
- ISO 10694: Soil Quality – Determination of organic and total carbon after dry combustion (elemental analysis). The direct combustion after acidification is commonly analyzed by resistance and induction furnace analyzers.

Methodology

C744/844

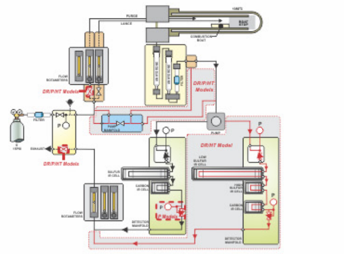
The C744/844 series carbon analyzer is an induction furnace system designed for the determination of carbon content of metals, ores, ceramics, and other inorganic materials.



A pre-weighed sample is placed in a crucible and combusted, with aid from a combustion accelerator, in a stream of purified oxygen using RF induction to heat the sample. Carbon present in the sample is oxidized to carbon dioxide (CO_2) and swept by the oxygen carrier through a heated dust filter and a drying reagent. The gas flow continues past a heated catalyst, where carbon monoxide (CO) is converted to CO_2. Carbon is then detected, as CO_2, by a non-dispersive infrared detection (NDIR) carbon detection cell.

C832

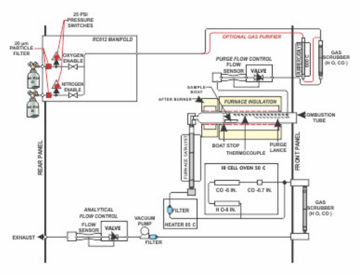
The C832 Series of elemental analyzers are resistance furnace systems designed to determine the carbon content in a wide variety of organic materials, as well as some inorganic materials, such as soils, cements, and limestone, by high-temperature combustion utilizing NDIR carbon detection.



Analysis begins when a sample is weighed into a combustion crucible and placed into the furnace which is typically regulated at 1350 °C with a pure oxygen environment. The sample combusts, releasing carbon as CO_2 gas. After a preset time, additional oxygen is introduced via a ceramic lance directly above the sample to accelerate the combustion of refractory materials. The combustion gases are swept to the back of the furnace and then forward through the inner and outer furnace tubes, allowing the combustion gases to remain in the high-temperature zone of the furnace, ensuring efficient oxidation. Upon exiting the furnace, the combustion gases flow through a drying agent and on to the flow controller, setting the flow of the combustion gases through the NDIR carbon detection cell.

RC612

The RC612 is a resistance furnace multiphase carbon and moisture determinator which quantifies the carbon and moisture present in various organic and inorganic samples, and illustrates the source of several types of carbon. The RC612 features a state-of-the-art furnace control system, which allows the temperature of the furnace to be stepped and ramped from near ambient to 1100 °C, in either oxidative or reductive carrier gas. The RC612 utilizes an afterburner furnace that ensures complete combustion of volatile species released at lower primary furnace temperatures.



For this application, the furnace is programmed with a two-step temperature ramping profile to separate organic and inorganic forms of carbon. Some materials contain multiple forms of organic carbon that may contribute to the premature release of inorganic carbon due to the exothermic combustion.

Background

Moisture

Expressing carbon content on a dry basis is a crucial factor in reporting accurate carbon results. It is recommended that samples be dried for 1 hour at 105 °C prior to analysis, or determine the moisture content on the day the samples are weighed for acid treatment for later dry basis correction of the carbon results. Moisture content of soil and rock materials is typically below 10%.

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 are more likely to absorb or be miscible with aqueous acid treatments. These materials can be analyzed without any prior treatment of 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 force 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 in the material.

Sample Pretreatment

All samples must be pulverized or ground until 100% of the material passes through a No. 100 (149 μm) sieve. For hydrophobic samples, the use of dilute surfactant (0.6 mL LECO 501-179 LECONAL per 50 mL distilled water) prior to the acid treatment process is required. LECO utilizes two independent methods of acid pretreatment for TOC determination on both induction and resistance furnace systems.

C744/844 Induction Furnace System

	Watch Glass Acid Pretreatment
1	Sample weighed onto a 2- to 3-inch watch glass
2	Add 0.25 mL of surfactant if necessary
3	Treated with 3N HCl
4	Dried in oven for one hour
5	Treatment repeated until no effervesce occurs
6	LECO 528-018 Ceramic Crucibles are pre-baked at 1000 °C for 40 min
7	Sample is scraped from watch glass to pre-baked 528-018 Ceramic Crucible
8	~1.5 g Tungsten and ~0.8 g Copper Accelerators are added to the sample
9	Sample is analyzed

	Disposable Glass Insert Acid Pretreatment
1	Disposable glass insert pre-baked at 600 °C for 60 min
2	Sample weighed into the glass insert
3	Add 0.25 mL of surfactant if necessary
4	Treated with 3N HCl
5	Dried in oven for one hour
6	Treatment repeated until no effervesce occurs
7	LECO 528-018 ceramic crucibles are pre-baked at 1000 °C for 40 min
8	Glass insert is placed into a pre-baked 528-018 Ceramic Crucible
9	~1.5 g Tungsten and ~0.8 g Copper Accelerators are added to the sample
10	Sample is analyzed

Table 1: Induction System Method Procedures

The first method utilizes a 2- to 3-inch watch glass for an acid treatment platform (shown in Figure 1). We are proposing a second method of sample analysis for the C744/844 utilizing a prototype disposable LECO glass crucible insert (shown in Figure 2), designed to be placed into a LECO 528-018 Ceramic Crucible.

Figure 1: Watch glass for acid treatment on both C744/844 and C832 systems.

Figure 2: Prototype glass crucible insert for C844/744 series induction systems.

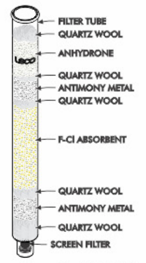


Figure 3: Halogen Trap Kit 619-592-150

Before samples are analyzed, a halogen trap must be installed to prevent damage to the instrument. LECO Trap Kit 619-592-150 (shown in Figure 3) should be used for the C844/744 series instruments. Then the instrument must have blank determinations as well as a calibration performed. The samples will have accelerator mixed with them to act as a combustion aid in the induction furnace. Treated samples should only contain organic carbon that, when combusted in a pure oxygen stream, is converted to CO_2 and subsequently detected by a NDIR cell. Spent samples are discarded with the crucible.

Typically, rock and ore TOC samples containing lower levels of organic matter can be analyzed on the induction furnace systems, resulting in a faster analysis time than the C832.

The induction furnace systems are not typically recommended for samples containing organic matter such as soil due to some organic matter-producing volatiles within the induction furnace prior to achieving maximum temperature. Volatiles are not detected by the infrared detectors and can also cause damage to the instrument should the volatiles ignite within the flow path. Organic compounds were included in the induction system analysis protocol for comparison purposes.

C832 Resistance Furnace System

	Watch Glass Acid Pretreatment
1	Sample weighed onto a 2- to 3-inch watch glass
2	Add 0.25 mL of surfactant if necessary
3	Treated with 3N HCl
4	Dried in oven for one hour
5	Treatment repeated until no effervesce occurs
6	LECO 528-203 Ceramic Crucibles are pre-baked at 1000 °C for 40 min
7	Sample is scraped from watch glass to pre-baked 528-203 Ceramic Crucible
8	Sample is analyzed

	Reusable Quartz Insert Acid Pretreatment
1	Reusable quartz insert is pre-baked at 1000 °C for 60 min
2	Sample weighed into the reusable quartz insert
3	Add 0.25 mL of surfactant if necessary
4	Treated with 6N HCl
5	Dried in oven for one hour
6	Treatment repeated until no effervesce occurs
7	LECO 528-203 Ceramic Crucibles are pre-baked at 1000 °C for 40 min
8	Quartz insert is placed into a pre-baked 528-203 Ceramic Crucible
9	Sample is analyzed

Table 2: Resistance Furnace Method Procedures

The determination of TOC on the C832 is performed using two methods similar to the induction system. The first method utilizes the watch glass (shown in Figure 1). The second method utilizes a reusable quartz insert (shown in Figure 4) that is reused a minimum of five times. Before samples are analyzed, a halogen trap must be installed according to LECO Product Information Bulletin 202-001-315 (shown in Figure 5).

Figure 4: Prototype quartz boat insert for C832 Series reistant systems.

Figure 5: LECO Product Information Bulletin 202-001-315

RC612 Ramping Resistance Furnace System

	Temperature Dependent Differentiation of Carbon
1	LECO 781-335 Quartz Boat is pre-baked at 1000 °C for 1 hour
2	Sample is weighed into the pre-baked 781-335 Quartz Boat
3	Sample is analyzed

Table 3: Ramping Resistance Furnace Method Procedure

For the purposes of TOC determination, the RC612 is configured to use a two-step temperature ramping analysis, at 450 °C and 1000 °C, without acid treatment. The LECO 781-335 Reusable Quartz Boats (shown in Figure 6) are designed specifically for the RC612 and differ from the quartz inserts used on the C832 Series instrument. These boats cannot be used interchangeably.

Figure 6: Reusable quartz boat 781-335

Results

Calibration

The C744 induction and C832 resistance furnace instrument were both calibrated using a 5.00% Synthetic Carbon (LECO 502-030 Lot: 1060) reference material and a single standard calibration forced through the origin. The RC612 ramping resistance furnace instrument was calibrated using the pure chemical Calcium Carbonate (LECO 501-034 Lot: 1043) and 1.00% Synthetic Carbon (LECO 502-029 Lot: 1109) reference material with a linear regression curve.

Verification

The C744 induction and C832 resistance furnace instrument's calibration and stability were verified using the pure chemical reference material 1.00% Synthetic Carbon (LECO 502-029 Lot: 1109). The RC612 ramping resistance furnace instrument's calibration was verified using a 0.53% Synthetic Carbon (LECO 502-630 Lot: 1011) and 5.00% Synthetic Carbon (LECO 502-030 Lot: 1060). The synthetic carbon was analyzed after the calibration and interspersed within the acid treated samples analysis sequence serving as a calibration and stability check sample. All verification reference materials were within the certified uncertainty for the carbon value with RSD <1.9%.

Sample Data

Sample suites were chosen for this study to demonstrate the analytical performance and application capability of the method configurations to determine TOC results based on furnace type and sample pretreatment. Where possible, materials with certified total carbon values were utilized to assess accuracy and precision.

LECO 502-062 Lot: 1018 n=5	C744		C832		RC612	Certified Carbon
% Total Carbon Avg	0.921		0.929		0.903	0.924
% Total Carbon Std Dev	0.012		0.002		0.003	0.025
	Watch Glass	Glass Insert	Watch Glass	Quartz Insert	Quartz Boat	
% Organic Carbon Avg	0.766	0.787	0.793	0.831	0.782	-
% Organic Carbon Std Dev	0.025	0.005	0.008	0.004	0.003	-
LECO 502-308 Lot: 1018 n=5	**C744**		**C832**		**RC612**	**Certified Carbon**
% Total Carbon Avg	2.37		2.41		2.37	2.42
% Total Carbon Std Dev	0.03		0.01		0.03	0.05
	Watch Glass	Glass Insert	Watch Glass	Quartz Insert	Quartz Boat	
% Organic Carbon Avg	2.06	2.17	2.21	2.29	2.18	-
% Organic Carbon Std Dev	0.10	0.02	0.02	0.01	0.04	-

Table 4: Hydrophilic Soils

LECO 502-309 Lot: 1012 n=5	C744		C832		RC612	Certified Carbon
% Total Carbon Avg	11.74		11.83		11.75	11.98
% Total Carbon Std Dev	0.14		0.03		0.09	0.44
	Watch Glass	Glass Insert	Watch Glass	Quartz Insert	Quartz Boat	
% Organic Carbon Avg	10.38	11.02	10.63	11.42	11.37	-
% Organic Carbon Std Dev	0.72	0.11	0.27	0.09	0.07	-
LECO 502-814 Lot: 1002 n=5	**C744**		**C832**		**RC612**	**Certified Carbon**
% Total Carbon Avg	22.2		22.4		22.5	22.6
% Total Carbon Std Dev	0.15		0.09		0.09	0.3
	Watch Glass	Glass Insert	Watch Glass	Quartz Insert	Quartz Boat	
% Organic Carbon Avg	18.7	21.2	20.2	21.4	21.3	-
% Organic Carbon Std Dev	0.77	0.09	0.16	0.06	0.08	-

Table 5: Hydrophobic Soil

The total carbon results for all furnace types produced results within the certified value and uncertainty for carbon with the exception of 502-814 on the C744. The differences in resistance furnace average organic carbon results with both the watch glass and quartz insert were statistically insignificant. The induction furnace organic carbon results suggest a noticeable recovery loss with the use of the insert relative to the resistance furnace results with the same. This is likely due to the loss of volatile gas during combustion. The results for the watch glass method for both furnace types compared to the respective insert results indicates significant recovery loss due to the transfer inefficiencies from the watch glass to the crucible. Insert based organic carbon results were 2 to 9 times more precise than that of the watch glass organic carbon results. Organic carbon results from hydrophilic soils exhibited similar trends as hydrophobic soils relative to furnace type and pretreatment method. The thermal differentiation results for both total carbon and organic carbon were consistent with both induction and resistance furnace system results.

The ore sample chosen in Table 6 was NIST SRM 886 due to the TOC information value on the certificate.

NIST SRM 886 n=5	C744		C832		RC612	Certified Carbon
% Total Carbon Avg	5.62		5.63		5.58	(5.7)
% Total Carbon Std Dev	0.03		0.01		0.02	-
	Watch Glass	Glass Insert	Watch Glass	Quartz Insert	Quartz Boat	
% Organic Carbon Avg	0.22	0.41	0.38	0.40	0.232	(0.3)
% Organic Carbon Std Dev	0.03	0.003	0.03	0.002	0.008	-

Table 6: Ore

Two samples of core drillings were selected to represent rock samples in Table 7.

Core Drilling 1 n=5	C744		C832		RC612	Certified Carbon
% Total Carbon Avg	11.0		11.1		11.3	-
% Total Carbon Std Dev	0.03		0.01		0.07	-
	Watch Glass	Glass Insert	Watch Glass	Quartz Insert	Quartz Boat	
% Organic Carbon Avg	10.7	10.9	10.7	10.9	11.1	-
% Organic Carbon Std Dev	0.09	0.05	0.09	0.03	0.07	-
Core Drilling 2 n=5	**C744**		**C832**		**RC612**	**Certified Carbon**
% Total Carbon Avg	14.9		14.9		15.0	-
% Total Carbon Std Dev	0.06		0.01		0.07	-
	Watch Glass	Glass Insert	Watch Glass	Quartz Insert	Quartz Boat	
% Organic Carbon Avg	14.4	14.7	14.3	14.7	14.7	-
% Organic Carbon Std Dev	0.13	0.02	0.09	0.02	0.07	-

Table 7: Core Drillings

The total carbon results for ore and core drillings were statistically consistent between all method configurations. The watch glass method indicated lower recovery compared to the crucible inserts of both furnace types, as well as the thermal differentiation method due to sample transfer loss. Insert based organic carbon results were 2 to 15 times more precise than that of the watch glass organic carbon results, consistent with the soil samples above.

Conclusion

Two sample preparation methods were employed for the induction and resistance furnace systems. In the case where samples were prepared using a watch glass versus a quartz or glass insert, the data indicates a high probability of sample loss while transferring the sample from the watch glass to the crucible. The quartz and glass inserts for both C832 and C744 showed increased recovery and precision due to treatment in the crucible, as no sample transfer is required. The use of a dilute surfactant solution when preparing hydrophobic soils for TOC determination is critical to achieving similar recovery and precision as with hydrophilic soils; no other biases were identified.

The C844/744 series instruments offer increased analysis speed, however, the C832 has the greatest flexibility when there is a need to analyze across multiple matrices for TOC determination. The C832 is the most flexible choice for the acid treated TOC application as it is able to analyze all samples without recovery loss. The resistance furnace design ensures that all carbon is converted to CO_2 during combustion with no matrix dependency.

The RC612 resistance furnace system utilized two different temperature set points to effectively separate the organic and inorganic carbon peaks without acid pretreatment. The RC612 obtained results consistent with the acid treatment methods, but due to the temperature ramping it also had the longest analysis time. This temperature differential method offers a semi-quantitative TOC determination without the lengthy sample pretreatment process.

Delivering the Right Results