SHIMADZU
Excellence in Science

TOC-L Total Organic Carbon Analyzer + SSM-5000A Solid Sample Combustion Unit

Application News

Evaluation of Total Organic Carbon Content of Biochar

Jiajie Du

User Benefits

- The total organic carbon (TOC) content of biochar can be determined by the difference between total carbon (TC) and inorganic carbon (IC) content.
- Both TC and IC can be measured easily and quickly, with each measurement taking approximately 10 minutes.
- Up to 30 mg of carbon can be quantified for TC measurements and up to 20 mg for IC measurements.

■ Introduction

Biochar is defined as a solid material produced by heating biomass to temperatures above 350 °C under controlled oxygen levels that prevent combustion. It is expected to have benefits such as soil improvement, increased agricultural productivity, and carbon sequestration in the soil.

In recent years, carbon sequestration using biochar has attracted attention as one of the technologies enabling carbon dioxide removal (CDR) from the atmosphere, resulting in active research in this field. In 2019, the IPCC (Intergovernmental Panel on Climate Change) improved the guidelines to include a method for calculating carbon sequestration resulting from the application of biochar to agricultural and grassland soils. Consequently, carbon sequestration with biochar has been globally recognized as a CDR technology.

Additionally, research and development of high-performance biochar that can achieve both high carbon sequestration efficiency and increased agricultural productivity is also underway to expand the use of biochar.

Such research requires the evaluation of the total organic carbon (TOC) content in biochar and the TOC solid sample measurement system, which consists of the Shimadzu TOC-L total organic carbon analyzer combined with an SSM-5000A solid sample combustion unit, can be utilized for that purpose.

This article presents an example of evaluating the TOC content of biochar using the Shimadzu TOC solid sample measurement system.

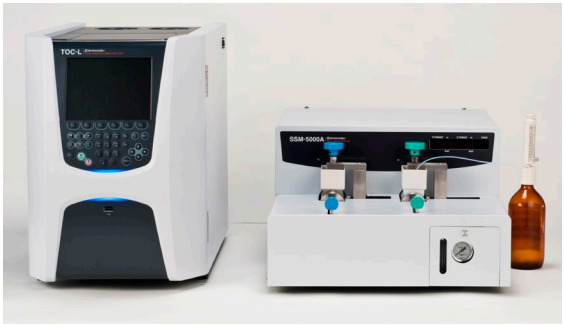


Fig. 1 TOC Solid Sample Measurement System
TOC-L Total Organic Carbon Analyzer (left) and SSM-5000A Solid Sample Combustion Unit (right)

■ TOC Solid Sample Measurement System

The TOC solid sample measurement system quantitates the carbon content by detecting the carbon dioxide released by either oxidizing solid samples at 900 °C for TC measurements or by acidifying samples with acid for IC measurements, which allows the TOC content to be determined from the difference.

Using this system, rapid, simple, and accurate analysis can be achieved by merely weighing the sample into a sample boat and placing it into the furnace. However, if the sample particle sizes are large, the reaction time will be longer or incomplete reactions may occur, leading to uneven reactions and affecting measurement accuracy. Therefore, it is necessary to pre-grind the samples finely and uniformly.

■ Analysis Method

Five types of biochar samples were prepared. Samples with large particle sizes were uniformly pre-ground using a mortar. Additionally, to remove moisture content, the samples were air-dried at room temperature for 24 hours.

Approximately 20 to 50 mg of each sample was placed in a sample boat for measurement.

For TC measurement, the sample boat was placed in the TC sample loading area (Fig. 2) and then inserted directly into the TC furnace.

For IC measurement, the sample boat with a small amount of pure water added was placed in the IC sample loading area (Fig. 3). After adding phosphoric acid using a dedicated dispenser, the sample was placed into the IC furnace.

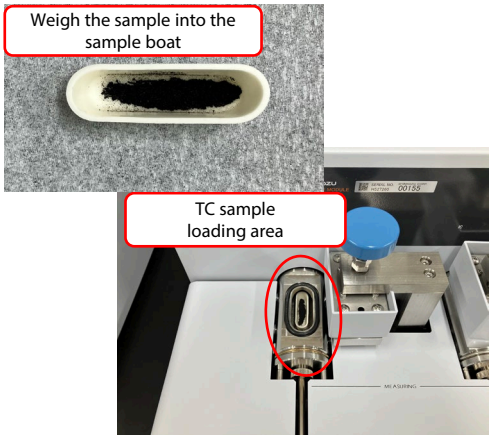


Fig. 2 TC Analysis

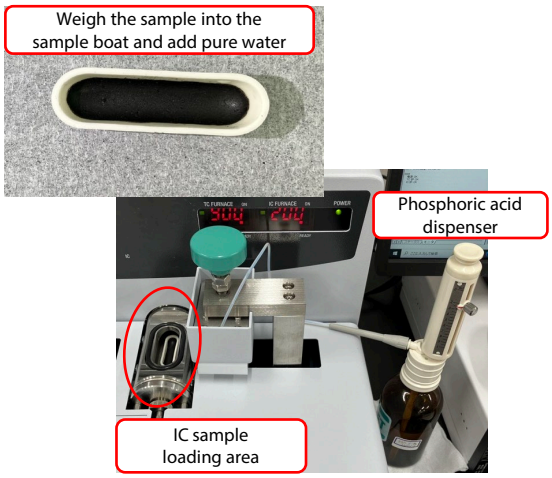


Fig. 3 IC Analysis

As a calibration curve sample, glucose powder reagent (carbon concentration 40 %) was used for TC measurement and sodium carbonate powder reagent (carbon concentration 11.3 %) was used for IC measurement. The measurement conditions are shown in Table 1.

Table 1 Measurement Conditions

Instrument	TOC solid sample measurement system (TOC-L_{CPH} total organic carbon analyzer + SSM-5000A solid sample combustion unit)
Cell Length	Short cell
SSM Carrier Gas	500 mL/min oxygen gas
TC Measurement Method	Combustion catalytic oxidation (TC furnace: 900 °C)
IC Measurement Method	Phosphoric acid acidification (IC furnace: 200 °C)
Measurement Item	TC, IC
Limit of Quantitation	100 µg (absolute carbon amount)
Calibration Curve	TC: One-point calibration curve using glucose powder reagent IC: One-point calibration curve using sodium carbonate powder reagent
Samples	Five types of biochar from different raw materials: Paper sludge biochar Chicken manure biochar Rice husk biochar Coconut shell biochar Coniferous wood biochar

■ Measurement Results

The measurement results for the five types of biochar are shown in Table 2 and examples of measurement data are shown in Fig. 4 (paper sludge biochar) and Fig. 5 (coconut shell biochar). It was found that the TOC concentration in biochar varied significantly depending on the raw materials, ranging from 17.2 % to 68.7 %. The coefficient of variation (CV) was less than 2 %, indicating good repeatability.

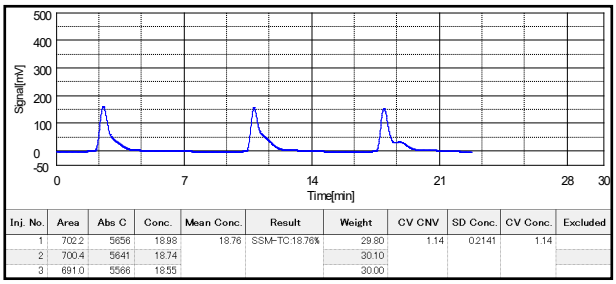
Additionally, the IC concentrations in rice husk biochar, coconut shell biochar, and coniferous wood biochar were below the limit of quantitation shown in Table 1 (absolute carbon amount of 100 µg) due to their low IC content.

Table 2 Measurement Results of Biochar

Samples	TC concentration [%] (CV)	IC concentration [%] (CV)	TOC concentration*1 [%]
Paper sludge biochar	18.8 (CV: 1.14 %)	1.58 (CV: 1.68 %)	17.2
Chicken manure biochar	41.8 (CV: 0.63 %)	1.24 (CV: 0.64 %)	40.5
Rice husk biochar	35.9 (CV: 0.61 %)	0.00*2	35.9
Coconut shell biochar	68.8 (CV: 0.63 %)	0.158*2	68.7
Coniferous wood biochar	66.3 (CV: 0.91 %)	0.0563*2	66.3

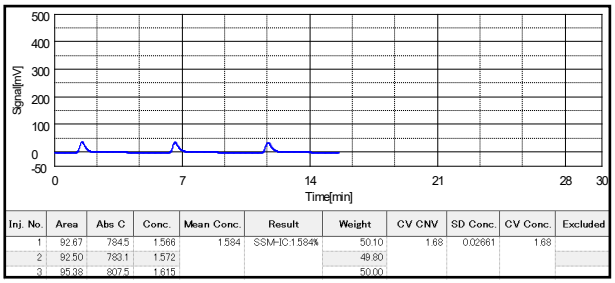
*1 TOC concentration = TC concentration – IC concentration

*2 Measurement value is below the limit of quantitation (absolute carbon amount < 100 µg)



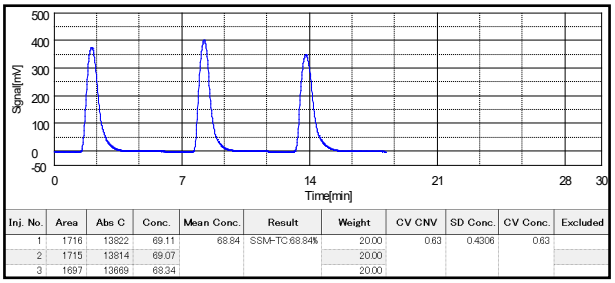
Inj. No.	Area	Abs C	Conc.	Mean Conc.	Result	Weight	CV CNV	SD Conc.	CV Conc.	Excluded
1	702.2	5656	18.98	18.76	SSM-TC:18.76%	29.80	1.14	0.2141	1.14	
2	700.4	5641	18.74			30.10				
3	691.0	5566	18.55			30.00				

Fig. 4-1 TC Measurement Data of Paper Sludge Biochar



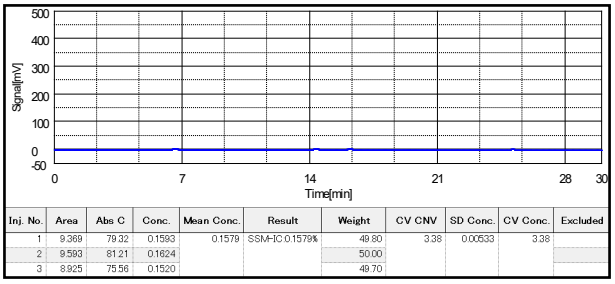
Inj. No.	Area	Abs C	Conc.	Mean Conc.	Result	Weight	CV CNV	SD Conc.	CV Conc.	Excluded
1	92.67	784.5	1.566	1.584	SSM-IC:1.584%	50.10	1.68	0.02661	1.68	
2	92.50	783.1	1.572			49.80				
3	95.38	807.5	1.615			50.00				

Fig. 4-2 IC Measurement Data of Paper Sludge Biochar



Inj. No.	Area	Abs C	Conc.	Mean Conc.	Result	Weight	CV CNV	SD Conc.	CV Conc.	Excluded
1	1716	13822	69.11	68.84	SSM-TC:68.84%	20.00	0.63	0.4306	0.63	
2	1715	13814	69.07			20.00				
3	1697	13669	68.34			20.00				

Fig. 5-1 TC Measurement Data of Coconut Shell Biochar



Inj. No.	Area	Abs C	Conc.	Mean Conc.	Result	Weight	CV CNV	SD Conc.	CV Conc.	Excluded
1	9.369	79.32	0.1593	0.1579	SSM-IC:0.1579%	49.80	3.38	0.00533	3.38	
2	9.593	81.21	0.1624			50.00				
3	8.925	75.56	0.1520			49.70				

Fig. 5-2 IC Measurement Data of Coconut Shell Biochar

■ Conclusion

By using the TOC solid sample measurement system, it is possible to measure both TC and IC, and the TOC can be determined from the difference in their concentrations.

In this article, the TOC concentrations of five types of biochar made from different raw materials were measured, which confirmed that the TOC concentrations varied significantly depending on the raw material. The CV value was less than 2 %, indicating good repeatability. This system, which can easily and quickly measure the TC and IC amounts of solid samples, is useful for measuring the TOC content of biochar.

Acknowledgment

We would like to express our sincere gratitude to TOWING Ltd. (https://towing.co.jp/pages/en) for their generous support in the creation of this application, including the provision of samples.

SHIMADZU

Shimadzu Corporation

www.shimadzu.com/an/

01-00730-EN First Edition: Jul. 2024