Application Note

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Abstract

The analysis of Total Organic Carbon (TOC) in samples can be difficult due to the variation of matrix types. Soil samples like sand, clay, and humus types can have erratic amounts of water, particle size, minerals, salt, and a large array of different materials depending on the collection location. The new Lotix Solid Sampler (LSS) Module used in conjunction with the Lotix High-Temperature Combustion TOC Analyzer will easily analyze a variety of difficult solid sample matrices accurately and reproducibly over a wide carbon concentration range.

Introduction

The LSS Module is an ideal add-on to the Lotix High Temperature Combustion Analyzer. The LSS enables the user to switch back and forth between liquid and solid samples in minutes with just a few quick connection changes.

The LSS uses an injector that holds a quartz sample boat capable of loading up to 1.5 grams of sample, depending on the matrix. The sample injector automatically moves the boat into the combustion zone of the furnace via the TekLink software. The combustion zone holds a vertical quartz tube packed with catalyst. The sample is heated to a temperature between 800°C and 1000°C and all carbonaceous matter is oxidized to CO_2.

The closed-system is flushed continuously with 200 cc/min of carrier gas. Once oxidized, the sample exits the LSS and is carried to the Lotix TOC Analyzer's Non-Dispersive Infrared Detector (NDIR) for analysis. The signal from the NDIR is integrated by the TOC TekLink software and displayed as analytical results in ppmC or µgC/g concentration units.

This study evaluates the LSS analyzing a wide variety of sample matrices including sand, soil, humus, and shot-blasting grit. Accuracy and precision based on % Relative Standard Deviations (RSD) were evaluated.

Experimental Instrument Conditions

The LSS uses a quartz combustion tube packed with pre-conditioned cobalt oxide catalyst for oxidation. The default "Solids" method in the TekLink software was used for this analysis.

Analytical Procedures

The following procedures used to conduct this study are shown below.

Standards Preparation

10,000 ppmC Stock Standard

1. A stir bar was added to the solution and mixed thoroughly.
2. 10.625 g of Potassium Hydrogen Phthalate (KHP) was measured into a tared weigh boat. The KHP was then added to a 500 ml volumetric flask filled half-way with deionized (DI) water. The flask was then brought to volume.

Note: Higher concentrations may require longer mixing times to ensure that all of the KHP is in solution.

Working Calibration Standards

Working calibration standards for a 7-point concentration range of 0 – 10,000 ppmC were created from the 10,000 ppmC stock standard using the recommended serial dilutions in Table 1.

Table I Working Calibration Standards		
Amount of Stock Std Pipette (ml)	**Brought to Volume (ml)**	**Final ppmC Concentration**
0	100	0.0
1	100	100.0
5	100	500.0
10	100	1000.0
25	100	2500.0
50	100	5000.0
100	100	10000.0

Calibration Curve

1. A calibration schedule was created using the default "Solids" method in TOC TekLink and included each of the calibration concentrations listed in Table I. Each calibration standard was analyzed in triplicate to verify the precision of the results.
2. Using a gas-tight syringe, 50 µL of the 0.0 ppmC standard was accurately injected onto a quartz boat packed with quartz wool. The boat was then placed on the sample boat carrier of the LSS sample injector.
3. When prompted by the software, the volume/weight of the sample was entered into TOC TekLink. Once entered, the software automatically moved the sample into the combustion furnace for analysis.
4. The procedure was repeated in triplicate for all remaining concentration levels to confirm reproducibility.
5. Once analysis of the calibration standards was complete, the calibration curve results were reviewed.

Acid Reagent Preparation for IC removal

An acid reagent was prepared for removing inorganic carbon from the samples by mixing a 1:1 ratio of nitric acid and DI water.

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Sample Preparation

1. Samples were ground, sieved, and mixed thoroughly prior to analysis to ensure homogeneity. The quantity of sample prepared was large enough to ensure the analysis of each sample in triplicate to verify the precision of the results.
2. Each sample was dried in an oven at 105 °C to remove any moisture.
3. Each sample was placed in a desiccator and cooled to ambient temperature.
4. Each sample was accurately weighed in a clean quartz boat and the weight recorded.
5. The prepared acid reagent was then added in a quantity sufficient to cover the entire sample and ensure complete IC removal (~5-100 µL)
6. After the acid addition, the sample was returned to the 105 °C oven and dried for approximately 5-10 minutes to remove any moisture. Once dried, the samples were then ready for analysis (Figure 1).

Sample Analysis

1. A sample schedule was created in TOC TekLink using the default "Solids" method. A mid-range calibration standard was added to the schedule to ensure the calibration curve was valid.
2. The quartz boat with solid sample was then placed on the LSS sample injector boat carrier.
3. When prompted by TOC TekLink, the volume/weight of the sample was entered. Once entered the software automatically moved the sample into the combustion furnace for analysis and the concentration calculated against the calibration curve.

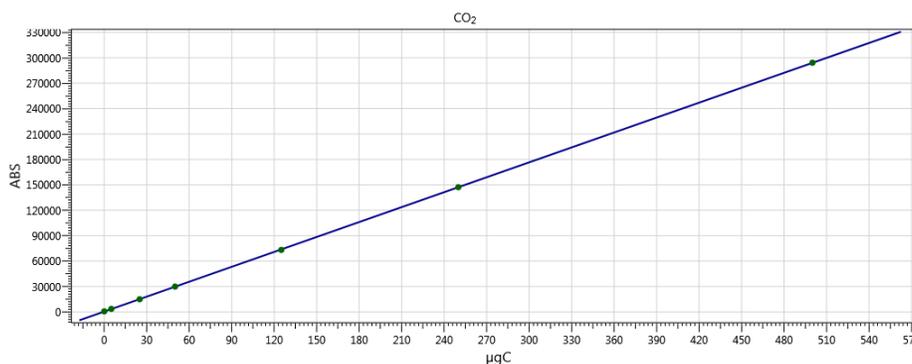**Figure 1**   Varying Sample Matrix Types Run on the LSS

Results

The 7-point calibration curve yielded an r^2 value of 0.99999 and the %RSD values for triplicate analyses are shown in Table II and Figure 2.

Table II Calibration Results	
Calibration Standard (ppmC)	**%RSD**
0.0	8.247
100.0	2.632
500.0	0.647
1000.0	0.732
2500.0	0.317
5000.0	0.494
10000.0	0.459

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Figure 2 Calibration Curve r^2 Value 0.99999

A known standard of carbon from the United States Geological Survey (USGS) was analyzed to determine the accuracy of the results. The USGS standard is 9.68% ± 0.45% or 92,300 – 101,300 ppmC. The known USGS soil standard showed that the LSS Module operated within the accepted standard range as seen in Table III.

Table III Accuracy Check Through Soil Standard n=3			
Soil Standard	**%RSD**	**Calculated ppmC**	**Accepted ppmC Range**
USGS	1.90	94,943.755	92,300 – 101,300

The samples used for this analysis had a concentration range from 1382 ppmC to 334,979 ppmC which indicates the LSS handles samples with a very wide concentration range as shown in Table IV.

Note: Sample absorbance (ABS) counts should be within the ABS counts of the calibration range. With high ppmC concentration samples, smaller sample sizes were used. If samples contain a lower ppmC concentration, then a larger sample size may be used.

Table IV Sample Results n=3		
Sample	**%RSD (Target <%5)**	**Average ppmC or mgC**
Sand	4.628	10,528
Dirt	1.429	42,988
Humus	4.520	334,979
Grit	0.621	1,382

Conclusion

The Teledyne Tekmar LSS is an ideal addition to the Lotix TOC Analyzer. The LSS generated less than 2% accuracy and less than 5% precision across standards and difficult-to-oxidize samples. Compact and simple, the LSS is designed to accurately measure carbon content in a variety of matrices making it the ultimate solution for all of your TOC needs.