

Total Organic Carbon Analysis of Solid Samples for Environmental and Quality Control Applications

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INTRODUCTION

Total Organic Carbon (TOC) analysis of solid samples provides useful information for environmental applications including waste management, biomass conversion, and carbon cycle research, as well as quality control (QC) checks of industrial materials such as fly ash, cement, and kaolin. The heterogeneous composition of some solid samples poses an analytical challenge. Matrix conditioning steps (e.g., sample drying, grinding, and pre-acidification to remove inorganic carbon) are often required to ensure complete oxidation of organic matter and an accurate TOC value is obtained.

This poster details design and performance characteristics of a new TOC solids analysis module and presents results of a validation study conducted using Standard Reference Materials (SRMs) and samples of unknown carbon content.

INSTRUMENT DESCRIPTION

The 1030S Solids Module is a sample preparation module that interfaces to an Aurora 1030 TOC Analyzer enabling analysis of the total organic carbon (TOC) or total carbon (TC) content in solid materials (Figure 1). The 1030S module oxidizes and converts the organic compounds in solid samples into CO₂ which is collected in a gas sampling device. When the combustion cycle is completed, CO₂ gas is transferred to the Aurora 1030 TOC analyzer for measurement by a non-dispersive infrared (NDIR) detector.

Solid samples to be analyzed are manually transferred and weighed in quartz crucibles. Two different volume crucibles are available (1 mL and 2.5 mL) to address differences in the mass, bulk density, and anticipated carbon content of samples.



Figure 1. 1030S Solids Module and Aurora 1030 TOC Analyzer

EXPERIMENTAL

A validation study was conducted using Standard Reference Materials (SRMs) and samples of unknown carbon content to assess the oxidation efficiency and TOC recoveries. Testing unknown samples for carbon recoveries enabled assessment of both inter-sample and intra-sample (replicates drawn from the gas sampling bag) variation. The three SRMs tested were SRM 2719 Calcined Petroleum Coke⁽¹⁾, SRM 8704 Buffalo River Sediment⁽²⁾, and SRM 2702 Inorganics in Marine Sediment⁽³⁾.

Two calibration ranges were required to account for differences in the carbon content of the various samples which ranged from 3 to 100% carbon. The low-level calibration was run on a system with the 1030S module interfaced to an Aurora 1030C combustion TOC Analyzer. The high-level calibration was run on a system with the 1030S module interfaced to an Aurora 1030W wet oxidation TOC analyzer.

Glucose and dextrose calibration solutions were dispensed into open-holed 1 mL crucibles using a 50 µL syringe. The syringe was flushed with DI water prior to aspiration of the sample to prevent carryover. Solid materials were weighed directly into the crucibles using a four-place balance. Quartz wool was placed in the bottom of all crucibles to help hold the samples. The crucibles were routinely conditioned to remove residual carbon and eliminate carryover.

The TC mode was used to analyze all samples in this study. Instrument operating conditions used for low- and high-level calibration settings are shown in Table 1.

Table 1. Instrument Operating Conditions for Low- and High-level Calibrations

Parameter	1030C TOC Analyzer Settings for Low-level Calibration	1030W TOC Analyzer Settings for High-level Calibration
Reaction Vessel Standby Temperature	35 °C	35 °C
Method	TC	TC
Sample (Gas Volume)	2 mL	2 mL
React (Combustion Time)	6 min	7 min
Detect (Time)	3 min	4 min
Furnace Temp	900 °C	900 °C
Crucible Conditioning Time	1.5	1.5
Sample Bag Purge Time	20 sec	45 sec
Purge Cycles	3	4

RESULTS & DISCUSSION

Calibration results showed a linear response at low and high levels. Both calibration curves had nearly identical R² values of 0.9988 for the lower range and 0.9990 for the higher range.

Once established, both curves were checked to ensure recoveries would be linear. The low-level calibration checks were run with 10% sucrose and 10% dextrose solutions. The high-level calibration checks were run using graphite. Results showed near 100% recoveries for all check standards.

Low-level Samples

Samples of known carbon content analyzed within the low-level calibration range included Buffalo River Sediment, Inorganic Marine Sediment, Urea, and Calcium Carbonate. Elliot Loam Silt⁽⁴⁾ was run to assess carbon recovery with Humic Acid.

Recoveries of 95% or better were obtained on all samples. Intra-sample testing (analysis of gas replicates) resulted in better than 2% RSD on three replicates. Average RSDs for inter-sample testing were better than 4% on three samples. Variation in inter-sample results with Elliot Loam Silt was likely due to inconsistencies in the sample itself. Further homogenization may be necessary to achieve more consistent results.

High-level Samples

Samples of known and unknown carbon content were run with the high-level calibration range. Calcined Petroleum Coke was used as a benchmark material for its nearly 100% carbon content (97.06%). Elliot Loam Silt was tested to compare recoveries obtained using both high- and low-level calibration ranges. Cellulose was used because it is a benchmark indicator of oxidation efficiency cited in several protocols, including EN 1484. Pure humic acid was also used as a test for complete oxidation because of its presence in many soil matrices. Finally, Fly Ash of unknown carbon content was used to test the consistency of oxidation of an uncharacterized material. The Fly Ash came in large chunks/fragments; a portion was crushed and ground into a fine powder using a mortar and pestle for homogeneity.

Slightly more variation was observed for samples tested using the higher level calibration curve. Calcined Petroleum Coke recovery was nearly 100%. Cellulose samples showed a matrix effect where smaller masses (< 19-mg C) exhibited more effective oxidation than larger masses (> 19-mg C). Elliot Loam Silt had a higher than expected recovery. Small variations in the calibration curve can affect measurements at the low end of the range. To ensure accurate recoveries are obtained analyses must be performed within the proper calibration range. Humic Acid showed approximately 90% recovery. The variation may be due to the fact the carbon content of humic acid is an estimated value. A true carbon value is difficult to obtain for this material even within the same sample. Accordingly, it is advisable that a SRM or other known sample be used to confirm recoveries of humic acid. The exact carbon content of the Fly Ash was unknown. Analysis of a SRM of similar composition yielded excellent recovery. Accordingly, the results of intra- and inter-sampling suggest high confidence in the Fly Ash results.

Intra-sampling of these high-level materials showed excellent consistency with RSDs below 2.5%. Inter-sampling showed even better precision with RSDs below 2% with the exception of Elliot Loam Silt.

Table 2. Analytical Results for Low-level Samples

Sample	%Carbon	Intra-sample %RSD	Inter-sample %RSD	Expected %C	%Recovery
Urea	19.93	1.46	0.48	19.98	99.7
Buffalo River Sediment	3.24	1.47	0.55	3.35	96.8
Inorganic Marine Sediment	3.25	0.69	1.39	3.36	96.8
Calcium Carbonate	11.55	1.88	3.06	11.99	96.3
Elliot Loam Silt	2.77	0.51	3.43	2.90	95.6

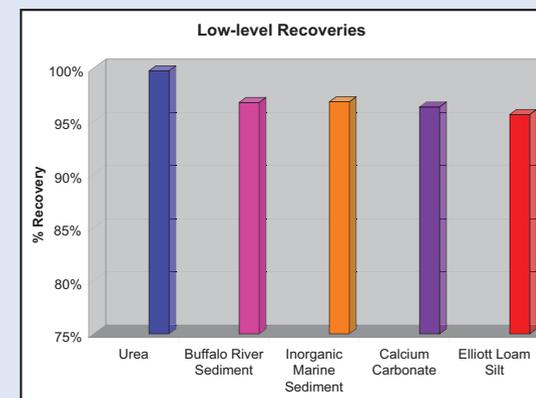


Figure 2. Low-level Recoveries

Table 3. Analytical Results for High-level Samples

Samples	%Carbon	Intra-sample %RSD	Inter-sample %RSD	Expected %C	%Recovery
Humic Acid	44.86	2.10	0.64	48.99	89.7
Calcined Petroleum Coke	96.33	1.72	1.02	97.06	99.2
Cellulose > 19 mg C	35.64	1.16	1.47	44.45	80.2
Cellulose < 19 mg C	42.10	1.71	1.87	44.45	94.7
Elliot Loam Silt	3.24	2.45	4.45	2.90	111.7
Fly Ash	40.04	0.91	1.04	unknown	—

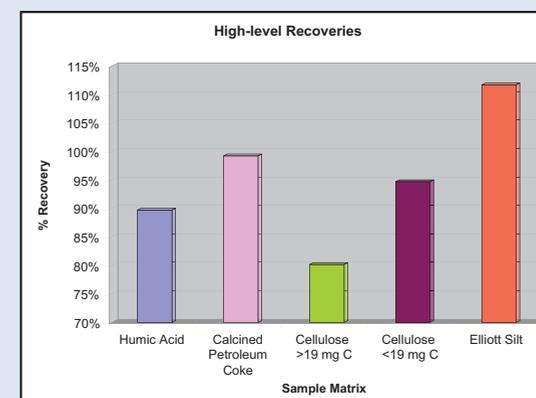


Figure 3. High-level Recoveries

SUMMARY & CONCLUSIONS

The results of analyses conducted using Standard Reference Materials demonstrate that the gas sampling device in the 1030S solids module is an effective mechanism for collecting the CO₂ produced during high temperature catalytic oxidation of solid samples for TOC analysis.

Total carbon recoveries obtained on low-and high-level samples using two calibration ranges achieved high-levels of accuracy and precision. RSDs for intra-sample testing (analysis of gas replicates) were below 2.5%. RSDs for inter-sample testing were generally below 4% not with standing issues with sample homogeneity.

Full details of the validation study are available in *OI Application Note #3514*⁽⁵⁾.

REFERENCES

- Standard Reference Material® 2719, Calcined Petroleum Coke, National Institute of Standards & Technology.
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