

Keywords

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

Introduction

Total Organic Carbon (TOC) analysis of solid samples provides useful information for environmental applications including waste management, biomass conversion, and carbon cycle research. TOC analysis is also used to perform quality control (QC) checks on industrial materials such as fly ash, cement, and kaolin. The heterogeneous composition of environmental samples poses an analytical challenge. Analytical methods (SW 846 Method 9060A and ISO 10694:1995) ^(1,2) describe matrix conditioning steps (e.g., sample drying, grinding, and pre-acidification to remove inorganic carbon) that are often required to ensure complete oxidation of organic matter and an accurate TOC value is obtained.

Existing techniques for TOC analysis of solids introduce the sample into a furnace for combustion. The resulting combustion gases are swept by a carrier gas stream from the furnace directly into a detector for measurement of CO₂ and calculation of the carbon content. This approach limits the sample mass that can be efficiently combusted and the measurable carbon range of samples. As a consequence, instruments operating on this principle are prone to over- and/or under-ranging the carbon content of materials being tested.

This application note details design and performance characteristics of a new sample preparation module for TOC analysis of solid samples that incorporates a gas sampling device to collect all CO₂ gas from combustion of each sample prior to transfer of a gas aliquot for measurement. Analytical results obtained on three Standard Reference Materials (SRMs), and humic acid, fly ash, and cellulose samples are reported.

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.

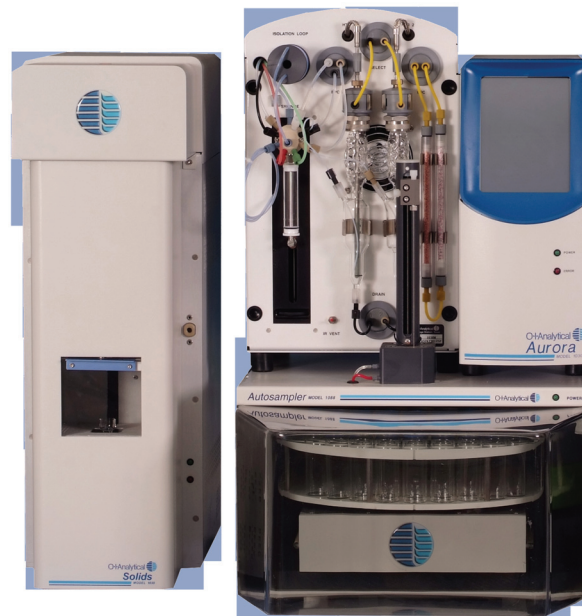


Figure 1. 1030S Solids Module and Aurora 1030 TOC Analyzer

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. These crucibles have either a solid bottom or a small diameter hole in the bottom.

Principle of Operation

The 1030S Solids Module supports two basic modes of operation for determining either the TOC or TC content of samples. The principal difference between the two modes lies in how the total inorganic carbon (TIC) content of samples is addressed. Accurate organic carbon analysis requires the capability to differentiate between inorganic and organic forms of carbon present in samples. Inorganic carbon is almost always present as carbonate minerals, either as calcium carbonate (calcite and/or aragonite), or as calcium magnesium carbonate (dolomite). All carbonate minerals are readily soluble in heated acid solution providing a means of distinguishing inorganic and organic carbon.

Operation for Total Organic Carbon Analysis

Determination of the TOC content requires a pre-acidification step to remove the TIC content of the sample prior to combustion in the 1030S. The solid sample to be analyzed is manually transferred and weighed in a quartz crucible. Adding acid to the crucible and heating the sample drives off CO_2 released from inorganic carbon compounds present in the sample.

The crucible with the TIC-free sample is then placed on the lift mechanism and raised into combustion tube of the 1030S module. The sample is heated to 500 °– 900 °C inside the furnace. Oxygen is introduced at a steady rate for high-temperature catalytic combustion. Organic matter in the sample is oxidized and converted to CO_2 gas which is collected in a 1 L capacity gas sampling bag. When the combustion cycle is completed, an aliquot of CO_2 gas is transferred from the gas sampling bag to the Aurora 1030 TOC analyzer for measurement by a solid state non-dispersive infrared (SSNDIR) detector. The result is reported as the TOC content in both mass and concentration of carbon. Analysis of combustion gas from a flexible sampling bag has advantages over direct injection to the detector. Specifically, greater control over combustion time is possible yielding an extended mass range while minimizing the effects of sample heterogeneity. Additionally, analysis of intra-sample replicates increases confidence in results.

Operation for Total Carbon Analysis

In total carbon analysis, the pre-acidification step to remove the TIC content is not required. The sample is manually transferred and weighed into a quartz crucible and placed directly on the 1030S lift mechanism. The subsequent sample combustion, CO₂ gas collection, transfer, and analysis steps are the same performed for TOC analysis. The mass of carbon reported is the total carbon (TC) content (TIC + TOC).

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 obtained with the 1030S Solids Module. 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 ⁽³⁾, SRM 8704 Buffalo River Sediment ⁽⁴⁾, and SRM 2702 Inorganics in Marine Sediment ⁽⁵⁾. Other samples tested included Humic Acid and Cellulose.

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 lower level calibration was run on a system with the 1030S module interfaced to an Aurora 1030C combustion TOC analyzer. The higher 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 sample-to-sample carryover.

Programming a method involves entering the sample mass, times for reaction and collection of combustion gas, and detection. 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

Table 2. 1030C and 1030W TOC Analyzer Calibration Results

Calibration	mg Carbon	Area	%RSD
Low-level (1030C) Calibration Results			
3 reps	0.5	7,042	0.51
	1	14,898	2.73
	2.5	34,603	2.81
	5	66,287	2.14
	10	127,460	1.67
Response Factor (RF)	–	0.0794	–
R²	–	0.9990	–
High-level (1030W) Calibration Results			
2 reps	11.1	71561	2.60
	19.9	133,081	1.98
	30.2	195,644	1.92
	39.7	260,628	1.61
	50.0	328,295	1.57
Response Factor (RF)		0.1523	–
R²	–	0.9988	–

Although samples falling within the lower level calibration range only require a 4 or 5 min combustion time (data not shown), a 6 minute combustion time was used for some hard to oxidize materials to assess combustion efficiency. A 7 minute combustion time was used for samples analyzed using the high-level calibration.

It should be noted that the purge times and number of purges were different for high and low level samples. At higher levels of carbon, larger purge volumes are recommended to ensure residual carbon is completely evacuated from the gas sampling bag.

Results and Discussion

Calibration results reported in Table 2 show a linear response at low and high levels. Both calibration curves had nearly identical R^2 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 lower 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.

Table 3. Low-level Calibration Curve Checks

Mass	mg	%Carbon	%RSD
Sucrose			
1 mg C	0.929	92.937	1.99
2.5 mg C	2.517	100.689	2.80
10 mg C	9.829	98.295	1.52
Dextrose			
1 mg C	0.913	91.273	2.82
2.5 mg C	2.595	103.788	2.90
10 mg C	10.041	100.410	0.66

Table 4. High-level Calibration Curve Checks

Mass	mg	%Carbon	%RSD
Graphite			
12.1 mg C	12.719	105.12	2.59
29.8 mg C	29.977	100.53	2.00
43.9 mg C	43.213	98.43	1.58

Low-level Samples

Samples of known carbon values were analyzed within the calibration range. These samples included two SRM standards - Buffalo River Sediment and Inorganic Marine Sediment, a typical additional validation standard of Urea, and Calcium Carbonate, an inorganic carbon standard. Additionally, a standard from the International Humic Substances Society (IHSS), Elliott Loam Silt ⁽⁶⁾, was run to assess carbon recovery with humic acid.

Recoveries better than 95% were obtained on all samples tested. Intra-sample testing, (analysis of gas replicates) resulted in better than 2% RSD on 3 replicates. Average RSDs for inter-sample testing were better than 4% on 3 samples. Variation in inter-sample results with Elliott Loam Silt were likely due to inconsistencies in sample-to-sample composition. Further homogenization may be necessary to achieve more consistent results.

Table 5. 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
Elliott Loam Silt	2.77	0.51	3.43	2.90	95.6

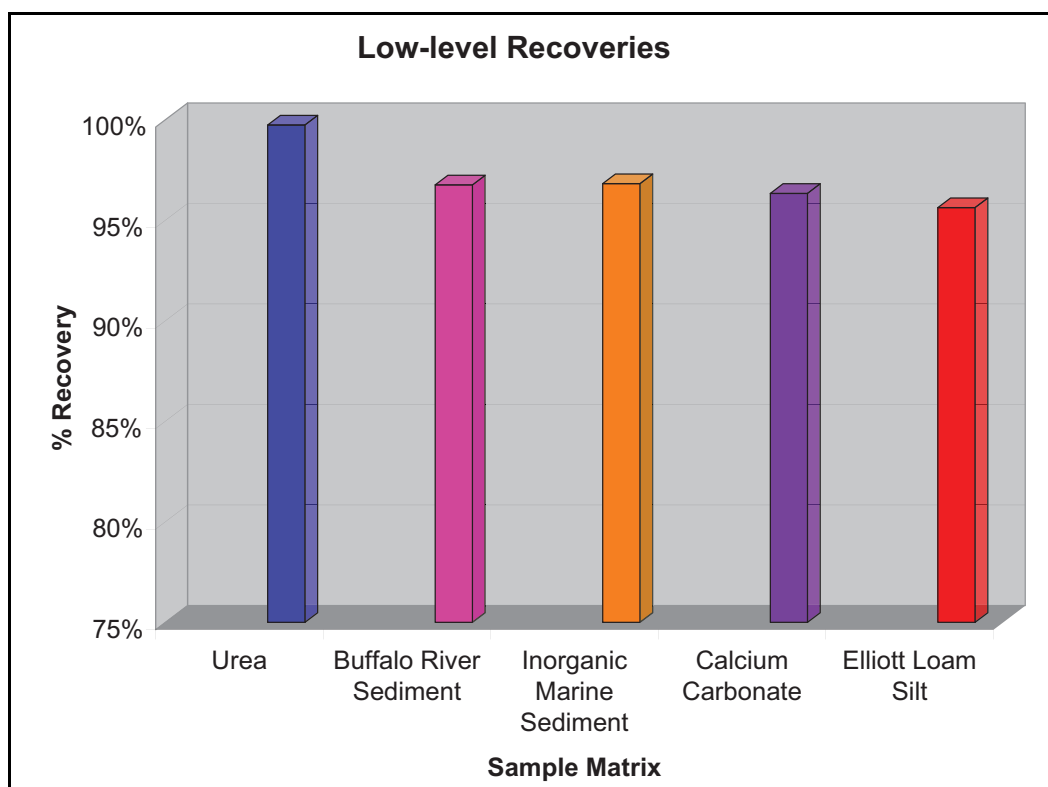


Figure 2. Low-level Recoveries

High-level Samples

In this sampling section, samples of known and unknown carbon content were run for comparison. Calcined Petroleum Coke was used as a benchmark material for its nearly 100% Carbon content (97.06%). Elliott Loam Silt was tested to compare recoveries obtained using both high and the low-level calibration ranges. Cellulose was used because it is considered the benchmark of oxidation efficiency in several protocols, including EN 1484⁽⁷⁾. Pure humic acid was also used as a test for complete oxidation because of its presence in many soil matrices. Finally, Fly Ash of an unknown carbon content was used to test the consistency of oxidation of an unknown compound. The Fly Ash material came in large chunks/fragments, a portion was crushed and ground into a fine powder using a mortar and pestle for homogeneity.

Table 6. 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
Elliott Loam Silt	3.24	2.45	4.45	2.90	111.7
Fly Ash	40.04	0.91	1.04	unknown	—

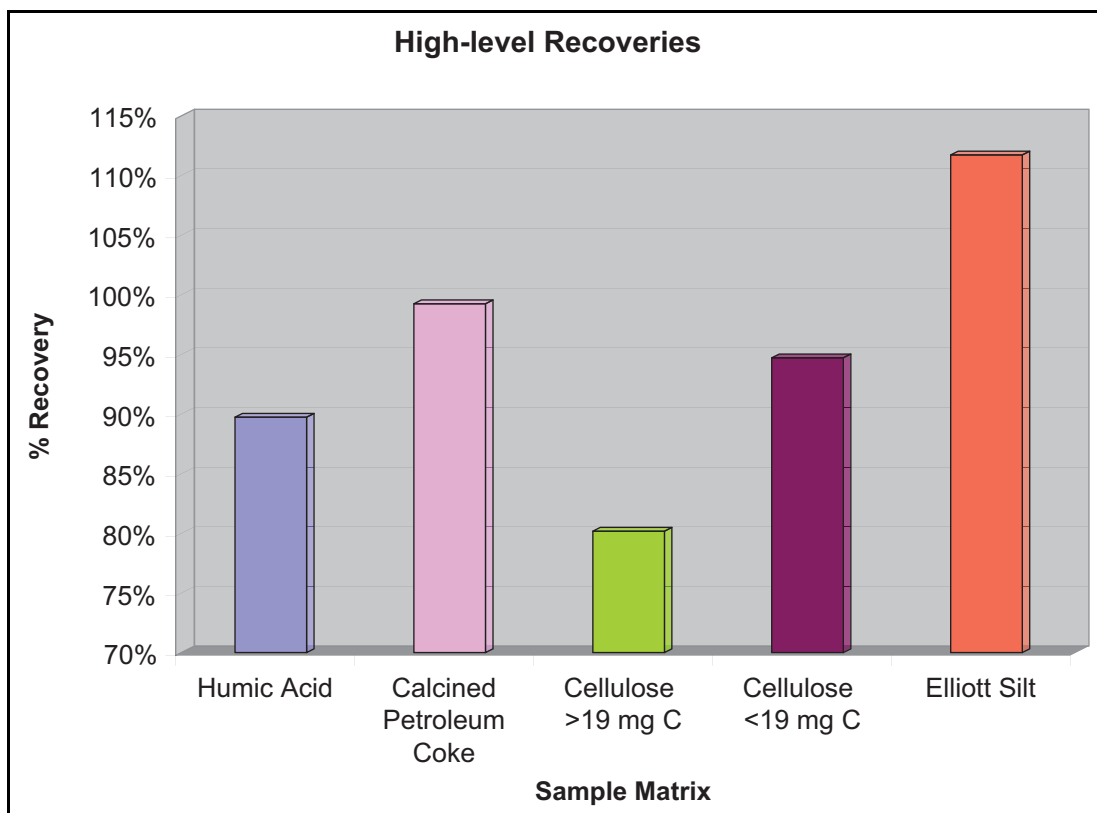


Figure 3. High-level Recoveries

Slightly more variation was observed for carbon content tested using the higher level calibration curve. Calcined Coke Petroleum recovery was nearly at 100%. Cellulose samples showed a matrix effect where smaller masses (<19 mg C) of cellulose exhibited more effective oxidation than larger masses (> 19 mg C). Elliott Loam Silt showed higher than expected recovery. Small variations in the calibration curve can affect low-level measurements. This can cause a positive or negative bias with masses outside the calibration range. To ensure accurate recoveries are obtained analyses must be performed within the proper range. Humic Acid showed approximately 90% recovery. Although the recovery is sufficient, 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. While the actual carbon content of the Fly Ash was unknown, because a SRM of similar composition showed excellent recovery, the results of intra- and inter- sampling suggest high confidence in the Fly Ash values.

When studying the efficiency of sampling techniques, overall intra-sampling of these materials showed excellent consistency below 2.5%RSD. Inter-sampling showed even better precision below 2%, with the exception of Elliott Loam Silt. This is most likely due to the absolute minimal recovery versus the amount of sample required for the calibration range.

Summary and Conclusions

The results of analyses conducted using Standard Reference Materials demonstrate that the gas sampling bag 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% notwithstanding issues with sample homogeneity.

References

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