Application Note

Instrument: CHN828

Determination of Carbon, Hydrogen, and Nitrogen in Biomass

LECO Corporation; Saint Joseph, Michigan USA

Introduction

Carbon, Hydrogen, and Nitrogen determination is part of the ultimate analysis of solid biofuel materials. Determining the content of these elements can help to characterize the materials and provide information that can be utilized in calculating material/energy balances. In addition, this information may be used to calculate efficiencies, as well as emissions potentials, for solid biofuel materials.

Instrument Model and Configuration

The LECO CHN828 is a combustion Carbon, Hydrogen, and Nitrogen determinator that utilizes a pure Oxygen environment in a vertical quartz furnace, ensuring complete combustion and superior analyte recovery. Combustion gases are swept from the furnace through an afterburner containing a reagent to scrub Sulfur compounds from the gas stream prior to collection in the ballast volume. The combustion gases are collected in a ballast where they equilibrate and mix before a representative aliquot (3 cm^3 or 10 cm^3 volume) of the gas is extracted and introduced into a flowing stream of inert gas (Helium or Argon) for analysis. The aliquot gas is carried to an infrared cell (IR) for the detection of Carbon (CO_2) and a thermal conductivity cell (TC) for the detection of Nitrogen (N_2). A separate portion of the ballast gas is transferred to an IR cell for the detection of Hydrogen (H_2O).

Thermal conductivity detectors work by detecting changes in the thermal conductivity of the analyte gas compared to a reference/carrier gas. The greater the difference between the thermal conductivity of the carrier gas and the analyte gas, the greater the sensitivity of the detector. The CHN828 supports either the use of Helium or Argon as the instrument's carrier gas. When used as a carrier gas, Helium provides the highest sensitivity, and the best performance at the lower limit of the Nitrogen range. Argon can also be used as a carrier gas. However, the thermal conductivity difference between Argon and Nitrogen is not as great as the thermal conductivity difference between Helium and Nitrogen, therefore the detector is inherently less sensitive when using Argon as a carrier gas.

Note: When changing carrier gas type, the flow needs to be adjusted following instructions provided in the 828 Series Operator's Instruction Manual.

Method Reference

ISO 16948: Solid Biofuels – Determination of Total Content of Carbon, Hydrogen, and Nitrogen.

Sample Preparation

Samples must be of a uniform consistency to produce suitable results. Reference materials should be prepared as directed by the certificate, prior to analysis.

Note: Carbon, Hydrogen, and Nitrogen results for biomass samples are typically reported on a dry basis in order to avoid reporting biases due to fluctuations in moisture levels. Therefore, either the material can be dried prior to analysis, or the moisture content can be determined on the day of analysis and entered into the instrument's software to correct for moisture. Biomass samples are typically dried at ~80 °C for 2 hours or until constant mass is achieved. The dried samples should be stored in a desiccator and must be used for analysis within 24 hours. For biomass reference materials, follow the sample drying instructions provided by the certificate.

Accessories

502-186 Tin Foil Cups, 501-441 Sucrose or commercially available Reagent Grade Sucrose (finely ground), and 501-614 Spatula

Reference Materials

LCRM®, LRM®, NIST, or other suitable reference materials.

Method Parameters*

Gas Type	Helium or Argon
Furnace Temperature	950 °C
Afterburner Temperature	850 °C
Nominal Mass	1.0000 g
Purge Cycles	3
Ballast Equilibrate Time	10 s
Ballast Not Filled Timeout	300 s
Aliquot Loop Fill Pressure Drop	200 mm Hg
Aliquot Loop Equilibrate Time	6 s
Interleave Analysis**	No
Sample Drop Detection	Disabled
Dose Loop Size[†]	Large (10 m^3) or Small (3 cm^3)

**Refer to the 828 Series Operator's Instruction Manual for Parameter definitions.*

***The Interleave Analysis feature was not utilized during the sample analysis performed to generate data for this application note. However, this feature may be utilized in order to increase sample throughput. Refer to the 828 Series Operator's Instruction Manual for Interleave Analysis definition.*

[†] The 10 cm^3 dose loop is recommended for this application when utilizing argon as a carrier gas. Due to the low Nitrogen levels typically found in biomass samples, it is not recommended that the 3 cm^3 dose loop be used when utilizing argon as a carrier gas, as the Nitrogen levels will be approaching the lower method detection limit.

Burn Profile

Burn Step	*Furnace Flow*	*Time*
1	5.00 L/min	30 s
2	1.00 L/min	30 s
3	5.00 L/min	End

Element Parameters[††]

	Helium			Argon		
Parameter	*Carbon*	*Hydrogen*	*Nitrogen*	*Carbon*	*Hydrogen*	*Nitrogen*
Integration Delay	4 s	‡	4 s	5 s	‡	5 s
Starting Baseline	15 s	‡	15 s	15 s	‡	15 s
Post Baseline Delay	0 s	‡	14 s	0 s	‡	15 s
Use Comparator	No	‡	No	No	‡	No
Integration Time	13 s	‡	35 s	16 s	‡	60 s
Use Endline	Yes	‡	Yes	Yes	‡	Yes
Endline Delay	19 s	‡	25 s	23 s	‡	30 s
Ending Baseline	15 s	‡	15 s	15 s	‡	15 s
Use Hydrogen Correction	--	Yes	--	--	Yes	–

[††] Refer to the 828 Series Operator's Instruction Manual for Parameter definitions.

[‡] Hydrogen determination is performed using a "stop-flow" analysis technique; therefore, the element parameters for Hydrogen are not adjustable.

Procedure

1. Prepare the instrument for operation as outlined in the operator's instruction manual.
2. Condition the System.
   a. Select five or more Blank replicates in the Login screen.
   b. Initiate the analysis sequence.
3. Determine Blank.
   a. Select five or more Blank replicates in the Login screen.
   b. Initiate the analysis sequence.
   c. Set the blank following the procedure outlined in the operator's instruction manual.

   Note: The standard deviation of the last five blanks should be less than or equal to 0.001% (10 ppm) for all three elements when utilizing Helium as a carrier gas, and less than or equal to 0.005% (50 ppm) for all three elements when utilizing Argon as a carrier gas. Additional blanks beyond the recommended five may be required in order to achieve the recommended precision.
4. Calibrate/Drift Correct.
   a. Select the desired number of calibration/drift replicates in the Login screen (minimum of five).
   b. Weigh an appropriate mass (~0.075 g to ~0.15 g) of a suitable reference material into a 502-186 Tin Foil Cup and seal the cup in a manner to minimize entrapped atmosphere by twisting the top edges of the foil together.
   c. Enter reference material mass and identification into the Login screen.
   d. Transfer the tin foil cup containing the reference material to the appropriate position in the sample carousel.
   e. Perform steps 4b through 4d a minimum of five times.
   f. Initiate the analysis sequence.
   g. Calibrate or Drift Correct the instrument following the procedure outlined in the operator's instruction manual.
   h. Verify the calibration/drift correction by analyzing an appropriate mass of another/different suitable reference material and confirm that the results are within the acceptable tolerance range.

   Note: Typically, the CHN828 can be calibrated using several replicates of a single mass range of a suitable reference material utilizing a linear, force through origin calibration. This is a cost-effective and simple process. A multi-point calibration (fractional mass or multiple calibration materials) may be used to calibrate if desired.
5. Analyze Samples.
   a. Select the desired number of sample replicates in the Login screen.
   b. Weigh an appropriate mass (~ 0.15 g) of the biomass sample into a 502-186 Tin Foil Cup and seal the cup in a manner to minimize entrapped atmosphere by twisting the top edges of the foil together.
   c. Enter sample mass and identification into the Login screen.
   d. Transfer the tin foil cup containing the sample to the appropriate position in the sample carousel.
   e. Perform steps 5b through 5d for each sample to be analyzed.
   f. Initiate the analysis sequence.
6. Atmospheric Blank Determination.

   Note: Some atmosphere may be trapped with the sample when it is encapsulated in the tin foil cup. This may cause biased Nitrogen results at low Nitrogen concentrations. Therefore, an atmospheric blank value may be determined and entered into the instrument's software to compensate for entrapped atmosphere using the following procedure.

   a. Select the desired number of sample replicates in the Login screen (minimum of 3).
   b. Weigh a similar mass (to the mass of the samples being analyzed) of an inert material such as 501-441 Sucrose or reagent grade sucrose (finely ground) into a 502-186 Tin Foil Cup and seal the cup in a manner to minimize entrapped atmosphere by twisting the top edges of the foil together.
   c. Enter the mass of the sucrose into the Login screen.
   d. Transfer the tin foil cup containing the sucrose to the appropriate position in the sample carousel.
   e. Perform steps 6b through 6d for each sucrose sample to be analyzed.
   f. Initiate the analysis sequence.
   g. The average Nitrogen value obtained is considered the atmospheric blank and can be automatically compensated for using the Instrument's software[‡‡].

[‡‡] Refer to the 828 Series Operator's Instruction Manual for details regarding the setting of the atmospheric blank.

TYPICAL RESULTS

Data was generated utilizing a linear, full regression calibration for Carbon determination, and linear, force through origin calibrations for Hydrogen and Nitrogen determination, using fractional masses (~0.07 g to ~0.15 g) of 502-642 (Lot 1019) LCRM Phenylalanine (65.47% C, 6.74% H, 8.46% N). The calibration was verified using LECO 502-896 (Lot 1003) LCRM EDTA (41.08% C, 5.52% H, 9.58% N). An atmospheric blank was determined using ground sucrose and was utilized to compensate for entrapped atmosphere. A moisture value for the samples was obtained utilizing a LECO TGM800 on the day of analysis and entered into the software to correct for moisture. Results are reported on a dry basis.

	Helium 10 cm^3				**Helium 3 cm^3**				**Argon 10 cm^3**			
	Mass (g)	*% C*	*% H*	*% N*	*Mass (g)*	*% C*	*% H*	*% N*	*Mass (g)*	*% C*	*% H*	*% N*
LECO 502-931 (Lot 1001)	0.1460	48.84	6.12	1.34	0.1450	48.62	6.18	1.40	0.1462	48.86	6.16	1.34
Orchard Leaves	0.1434	48.76	6.16	1.35	0.1459	48.39	6.22	1.38	0.1567	48.88	6.15	1.34
Carbon: 48.62% ±0.26%	0.1427	48.77	6.17	1.35	0.1457	48.83	6.22	1.35	0.1468	48.87	6.23	1.33
Hydrogen: 6.18% ±0.06%	0.1418	48.76	6.15	1.35	0.1530	48.69	6.22	1.35	0.1476	48.80	6.20	1.35
Nitrogen: 1.37% ±0.03%	0.1490	48.88	6.12	1.36	0.1501	48.86	6.11	1.35	0.1486	48.83	6.16	1.34
	Avg =	***48.80***	***6.14***	***1.35***	***Avg =***	***48.68***	***6.19***	***1.37***	***Avg =***	***48.85***	***6.18***	***1.34***
	s =	***0.06***	***0.02***	***0.01***	***s =***	***0.19***	***0.05***	***0.02***	***s =***	***0.03***	***0.03***	***0.01***
Corn Grain for Ethanol	0.1469	45.53	6.41	1.29	0.1539	45.67	6.50	1.29	0.1509	45.62	6.47	1.24
	0.1473	45.53	6.40	1.29	0.1502	45.70	6.56	1.29	0.1539	45.58	6.44	1.27
	0.1472	45.61	6.40	1.28	0.1525	45.66	6.53	1.29	0.1462	45.67	6.54	1.30
	0.1439	45.63	6.41	1.30	0.1447	45.53	6.60	1.27	0.1479	45.64	6.49	1.28
	0.1436	45.68	6.42	1.29	0.1430	45.62	6.61	1.28	0.1452	45.65	6.45	1.26
	Avg =	***45.60***	***6.41***	***1.29***	***Avg =***	***45.64***	***6.56***	***1.28***	***Avg =***	***45.64***	***6.48***	***1.27***
	s =	***0.07***	***0.01***	***0.01***	***s =***	***0.06***	***0.05***	***0.01***	***s =***	***0.03***	***0.04***	***0.02***
Biomass Fuel	0.1536	49.40	6.01	0.43	0.1558	49.35	6.05	0.44	0.1492	49.30	6.08	0.40
(Wood Chips/Sawdust)	0.1497	49.36	6.00	0.41	0.1503	49.49	6.07	0.41	0.1572	49.30	6.00	0.37
	0.1476	49.36	6.04	0.46	0.1540	49.46	6.10	0.39	0.1476	49.07	6.05	0.40
	0.1520	49.38	6.00	0.42	0.1485	49.52	6.10	0.43	0.1414	49.34	6.12	0.39
	0.1524	49.11	5.95	0.43	0.1432	49.58	6.11	0.44	0.1445	49.29	6.10	0.39
	Avg =	***49.32***	***6.00***	***0.43***	***Avg =***	***49.48***	***6.09***	***0.42***	***Avg =***	***49.26***	***6.07***	***0.39***
	s =	***0.12***	***0.03***	***0.02***	***s =***	***0.08***	***0.02***	***0.02***	***s =***	***0.11***	***0.05***	***0.01***

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