Application Note

Instrument: CHN828

Determination of Carbon, Hydrogen, and Nitrogen in Hydrocarbons

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Introduction

Carbon, hydrogen, and nitrogen determination is part of the ultimate analysis of hydrocarbon materials, helping to characterize the materials and provide information that can be utilized in calculating material/energy balances and efficiencies, as well as emissions potentials if the material is utilized as a fuel. The carbon, hydrogen, and nitrogen results for oil materials are also utilized to evaluate the refining potentials and yields in the petrochemical industry.

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 determination of hydrogen (H_2O).

Method Reference

ASTM D5291: Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants.

Note: A modified version of ASTM D5291 was followed to generate data for this application note. The test methods contained within ASTM D5291 indicate that capsules should be crimped closed with forceps. LECO has determined that sealing capsules closed entraps atmosphere with the sample, which can cause biased nitrogen results at low nitrogen concentrations. Therefore, the tin capsules used to generate data for this application note were left open and were not crimped closed so that atmosphere could be purged from the capsule while in the purge chamber.

Sample Preparation

Samples must be of a uniform consistency to produce suitable results.

Reference Materials

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

Method Parameters†

Gas Type	Helium
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
Dose Loop Size	Large (10 cm^3)
Interleave Analysis	Yes
Sample Drop Detection	Disabled

Note: Due to the low levels of nitrogen in this sample matrix, the use of a 3 cm^3 dose loop and argon as a carrier gas are not recommended.

Element Parameters†

	Carbon	*Hydrogen*	*Nitrogen*
Integration Delay	4 s	††	3 s
Starting Baseline	15 s	††	15 s
Post Baseline Delay	0 s	††	14 s
Use Comparator	No	††	No
Integration Time	13 s	††	35 s
Use Endline	Yes	††	Yes
Endline Delay	19 s	††	25 s
Ending Baseline	15 s	††	15 s
Use Hydrogen Correction	—	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.*

Burn Profile

Burn Step	*Furnace Flow*	*Time*
1	5.00 L/min	30 s
2	1.00 L/min	60 s
3	5.00 L/min	End

Accessories

502-186 Small Tin Foil Cups*, or 502-040 Small Tin Capsules, or 501-571 Copper Capsules with 502-008 Tin Plugs** (for use with volatile samples), 501-427 COM-AID (For Liquids), 502-901 Paraffin Oil (for atmospheric blank determination), disposable pipettes, and 501-614 Spatula

Sample Container	Comments	Instructions for Sample and COM-AID Addition	Atmospheric Blank
502-186 Small Tin Foil Cups*	• Recommended for oils with a medium to high viscosity such as lubrication oils, motor oils, or gear lubricants	1. Add ~0.2 g of COM-AID to the foil cup prior to adding the sample. Create a small depression (crater) in the center of the COM-AID and tare the balance. 2. Using a pipette, weigh/add the sample into the depression in the COM-AID. 3. Enter sample mass and identification into the Login Screen and tare the balance. 4. Cover the sample with an additional ~0.1 g of COM-AID. 5. Seal the tin foil cup closed by twisting the top edges of the foil together. 6. Refer to the Tin Foil Cups* footnote below for additional details regarding the addition of COM-AID.	• May require the use of an Atmospheric Blank • Refer to Section 6 of the Procedure for details and instructions regarding the use of an Atmospheric Blank
502-040 Small Tin Capsules	• Can be used with any type of hydrocarbon sample • Recommended for oils with a low volatility such as food oils or mineral oils	1. Using a pipette, weigh/add the sample into the tin capsule. 2. Enter sample mass and identification into the Login Screen and tare the balance. 3. Add ~0.3 g of COM-AID to the tin capsule, covering the sample. 4. Leave the capsule open so that atmosphere will be purged from the capsule while in the purge chamber.	• Does not require the use of an Atmospheric Blank
501-571 Copper Capsules**	• Used in conjunction with 502-008 Tin Plugs • Recommended for volatile oil samples such as diesel fuel • Will require frequent furnace crucible replacement • Refer to Copper Capsules** footnote below for additional details regarding furnace crucible replacement	1. Using a pipette, weigh/add the sample into the copper capsule. 2. Enter sample mass and identification into the Login Screen and tare the balance. 3. Add ~0.3 g of COM-AID to the copper capsule, covering the sample. 4. Seal capsule closed by gently securing a 502-008 Tin Plug into the opening of the copper capsule.	• May require the use of an Atmospheric Blank • Refer to Section 6 of the Procedure for details and instructions regarding the use of an Atmospheric Blank

Note: The use of 501-427 COM-AID results in a high ash load. Therefore, the furnace crucible (614-961-110 Porous Reticulated Crucible) fills up quickly with combustion residue, and as a result will need to be replaced frequently (Approximately every 100 analyses).

**When using tin foil cups, oil samples (especially those with a low viscosity) may tend to "wick" up the sides of the foil cup due to capillary action along the creases of the foil cup. This can make it difficult to seal the foil cup without losing some of the sample. This can be mitigated through the addition of ~0.2 g of 501-427 COM-AID to the tin foil cup prior to adding the oil sample. Create a small depression (crater) in the center of the COM-AID and tare the balance. Then add/weigh the oil sample into the depression in the COM-AID. This will help to absorb and contain the oil sample. After entering the sample mass into the Login Screen, tare the balance and add an additional ~0.1 g of COM-AID on top of the sample, and seal the foil cup by twisting the top edges of the foil together.*

***Copper Capsules and Tin Plugs oxidize completely, forming oxides, which results in a relatively high ash load. Therefore, the furnace crucible (614-961-110 Porous Reticulated Crucible) fills up quickly with combustion residue, and as a result will need to be replaced frequently (Approximately every 30 analyses).*

Procedure

1. Prepare the instrument for operation as outlined in the operator's instruction manual.
2. Condition the System.
   a. Select three to five replicates in the Login screen.
   b. Following the instructions contained within Table 1 of the Accessories Section, weigh an appropriate mass (~0.07 g to ~0.09 g) of a hydrocarbon reference or sample material into a sample container of choice, and add 501-427 COM-AID accordingly.
   c. Transfer the sample container with the conditioning sample and COM-AID to the appropriate position in the sample carousel.
   d. Perform steps 2b through 2c for each conditioning sample to be analyzed.
   e. Initiate the analysis sequence.
3. Determine Blank.
   a. Select five or more Blank replicates in the Login screen.
   b. Initiate the analysis sequence (No sample container is required for Blank determination).
   c. Set the blank using at least five blank results 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. 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 (~0.07 g to ~0.14 g) of a suitable reference material into a 502-186 Tin Foil Cup and seal the cup 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 for each reference material to be analyzed (minimum of five).
   f. Initiate the analysis sequence.
   g. Calibrate the instrument following the procedure outlined in the operator's instruction manual.
   h. Verify the calibration by analyzing several replicates of an appropriate mass of another/different reference material, following steps 4b through 4f, 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. Sample Analysis.
   a. Select the desired number of sample replicates in the Login screen.
   b. Following the instructions contained within Table 1 of the Accessories Section, weigh an appropriate mass (~0.07 g to ~0.09 g) of the sample into a sample container of choice, and add 501-427 COM-AID accordingly.
   c. Transfer the sample container with the sample and COM-AID to the appropriate position in the sample carousel.
   d. Perform steps 5b through 5c for each sample to be analyzed.
   e. 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 or copper capsule. This may cause biased nitrogen results at low nitrogen concentrations. Therefore, if using tin foil cups or copper capsules, an atmospheric blank may be determined and utilized to compensate for entrapped atmosphere following the procedure below. If tin capsules are being used, they should be left open so that atmosphere can be purged from the capsule when in the purge chamber, eliminating the need to compensate for entrapped atmosphere.
   a. Select the desired number of atmospheric blank sample replicates in the Login screen (minimum of 3).
   b. Following the instructions contained within Table 1 of the Accessories Section, weigh a similar mass (to the mass of the samples being analyzed) of 502-901 Paraffin Oil into a 502-186 Tin Foil Cup, or a 501-571 Copper Capsule (use the same sample container as was used for sample analysis) and add 501-427 COM-AID accordingly.
   c. Transfer the sample container with the oil sample and COM-AID to the appropriate position in the sample carousel.
   d. Perform steps 6b through 6c for each oil sample to be analyzed.
   e. Initiate the analysis sequence.
   f. The average nitrogen value obtained is considered the atmospheric blank and can be used to compensate for entrapped atmosphere utilizing the CHN828 software.

   Note: Refer to the 828 Series Operator's Instruction Manual for details regarding the setting of the atmospheric blank.

TYPICAL RESULTS

Data was generated utilizing linear, full regression calibrations for carbon and hydrogen determination, using fractional masses (~0.075 g to ~0.14 g) of LECO 502-642 (Lot 1018) Phenylalanine LCRM (65.46% C, 6.77% H). A linear, force through origin calibration was utilized for nitrogen determination, using fractional masses (~0.075 g to ~0.14 g) of LECO 502-642 (Lot 1018) Phenylalanine LCRM (8.47% N). The calibrations were verified using LECO 502-897 (Lot 1002) BBOT LCRM (72.55% C, 6.13% H, 6.52% N).

	502-186 Tin Foil Cup‡				**502-040 Tin Capsule**				**501-571 Copper Capsule with 502-008 Tin Plug‡**			
	Mass (g)	*% C*	*% H*	*% N*	*Mass (g)*	*% C*	*% H*	*% N*	*Mass (g)*	*% C*	*% H*	*% N*
Residual Oil	0.0648	83.74	13.18	0.072	0.0720	83.84	13.13	0.090	0.0701	83.62	13.22	0.071
LECO 502-850	0.0640	83.47	13.18	0.073	0.0628	83.86	13.21	0.075	0.0688	83.19	13.20	0.078
Lot# 1003	0.0672	83.44	13.17	0.073	0.0636	83.92	13.21	0.085	0.0715	83.77	13.21	0.076
83.86% ±0.71% C	0.0649	83.40	13.17	0.057	0.0671	83.79	13.21	0.087	0.0707	83.43	13.20	0.084
13.11% ±0.11% H	0.0624	83.29	13.16	0.063	0.0610	83.40	13.14	0.078	0.0691	83.41	13.20	0.065
0.07% ±0.03% N	***Avg =***	***83.47***	***13.17***	***0.067***	***Avg =***	***83.76***	***13.18***	***0.083***	***Avg =***	***83.48***	***13.21***	***0.075***
	s =	***0.17***	***0.01***	***0.007***	***s =***	***0.21***	***0.04***	***0.006***	***s =***	***0.22***	***< 0.01***	***0.007***
Paraffin Oil LCRM	0.0647	86.26	14.06	‡‡	0.0747	86.31	13.93	‡‡	0.0627	86.03	14.08	‡‡
LECO 502-901	0.0659	86.54	14.09	‡‡	0.0738	86.41	13.99	‡‡	0.0683	86.29	14.05	‡‡
Lot# 1001	0.0646	86.31	14.09	‡‡	0.0803	86.25	13.93	‡‡	0.0696	86.78	13.90	‡‡
86.4% ±0.5% C	0.0684	86.41	14.05	‡‡	0.0740	86.34	14.02	‡‡	0.0645	86.17	14.09	‡‡
14.0% ±0.1% H	0.0642	86.40	14.10	‡‡	0.0718	86.34	14.00	‡‡	0.0688	86.42	13.97	‡‡
	Avg =	***86.38***	***14.08***	***--***	***Avg =***	***86.33***	***13.98***	***--***	***Avg =***	***86.34***	***14.02***	***--***
	s =	***0.11***	***0.02***	***--***	***s =***	***0.06***	***0.04***	***--***	***s =***	***0.28***	***0.08***	***--***
Mineral Oil LSUS	0.0672	84.20	14.20	‡‡	0.0718	85.01	14.09	‡‡	0.0631	84.50	14.15	‡‡
LECO 502-922	0.0695	84.28	14.18	‡‡	0.0695	84.98	14.09	‡‡	0.0623	84.49	14.18	‡‡
Lot# 1001	0.0718	84.56	14.15	‡‡	0.0655	84.85	14.12	‡‡	0.0674	84.74	14.13	‡‡
	0.0650	84.54	14.26	‡‡	0.0743	84.90	14.06	‡‡	0.0627	84.32	14.17	‡‡
	0.0639	84.21	14.19	‡‡	0.0670	84.80	14.07	‡‡	0.0697	84.71	14.06	‡‡
	Avg =	***84.36***	***14.19***	***--***	***Avg =***	***84.91***	***14.09***	***--***	***Avg =***	***84.55***	***14.14***	***--***
	s =	***0.18***	***0.04***	***--***	***s =***	***0.09***	***0.02***	***--***	***s =***	***0.17***	***0.05***	***--***

‡An atmospheric blank value was determined and utilized to compensate for entrapped atmosphere using the instrument's software.
‡‡Nitrogen values were below the lower detection limit of the instrument.

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