Application Note

Instrument: CN928

Determination of Carbon and Nitrogen in Carbon Black and Graphite

LECO Corporation; Saint Joseph, Michigan USA

Introduction

Carbon black is a material produced by the incomplete combustion or thermal decomposition of petroleum products such as ethylene cracking tar, vegetable matter, or other hydrocarbons under controlled process conditions. Carbon black is used as a reinforcing filler in tires, as well as in belts, hoses and other non-tire rubber products. It is used as a color pigment in paints, plastics, coatings, and printing inks. The total Carbon content of Carbon black is a requirement for the calculation and reporting of Carbon dioxide emissions. It can also be used in calculations to estimate the yield of the process. Determining Nitrogen content helps Carbon black manufacturers ensure the quality and consistency of Carbon black production. Nitrogen levels are used in the optimization of the production process and are an indicator of the presence of desirable char structures.

Graphite is a crystalline form of the element Carbon, consisting of stacked layers of graphene. It is a stable form of Carbon that exists in nature, or it can be synthetically produced. Graphite has many applications in our daily lives including its use in pencils, lubricants, electrodes, batteries, and Carbon fiber. The determination of Carbon content in graphite is used to determine the purity of graphite materials and is a general indicator of the quality and material properties, including electrical conductivity and lubrication capabilities. Carbon determination is also used by graphite producers to monitor and optimize the graphitization process to ensure the desired graphite quality and material properties. Nitrogen determination in graphite materials provides insight into the material's catalytic potential for use in fields such as energy conversion and environmental protection.

Instrument Model and Configuration

The LECO CN928 is a macro combustion Carbon and Nitrogen determinator that utilizes a pure Oxygen environment in a high-temperature horizontal ceramic combustion furnace, utilizing ceramic boats designed to handle macro sample masses. A thermoelectric cooler removes moisture from the combustion gases before they are collected in a ballast. The gases equilibrate and mix in the ballast 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 carrier gas (Helium or Argon) for analysis. The aliquot of gas is carried through a heated reduction tube, filled with Copper, to convert Nitrogen Oxide combustion gas species (NO_x) to Nitrogen (N_2). The aliquot gas is then carried to a non-dispersive infrared (NDIR) cell for the detection of Carbon (as CO_2) and a thermal conductivity cell (TC) for the detection of Nitrogen (N_2).

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 CN928 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. 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.

The LECO CN928 offers the additional advantage of utilizing either a 10 cm^3 aliquot loop or a 3 cm^3 aliquot loop within the instrument's gas collection and handling system. The 10 cm^3 aliquot loop optimizes the system for the lowest Nitrogen range and provides the best precision. The 3 cm^3 aliquot loop extends reagent life expectancy by approximately three-fold when compared to the 10 cm^3 aliquot loop, while providing the lowest cost-per-analysis with minimal impact on practical application performance.

Note: When changing carrier gas type, the flow needs to be adjusted following instructions provided in the 928 Series Operator's Instruction Manual. The aliquot loop size is changed by selecting the desired aliquot loop size in the software's Method Parameters.

*Method Reference**

ASTM D7633: Standard Test Method for Carbon Black - Carbon Content.

**A modified version of ASTM D7633 Method was utilized for the generation of data included in this application note.*

Sample Preparation

Samples must be of a uniform consistency to produce suitable results. In accordance with ASTM D7633, Carbon black samples should be dried at ~125 °C for at least one hour prior to analysis. Graphite samples should be dried at ~105 °C for one hour prior to analysis. The dried samples should be stored in a desiccator and must be used for analysis within 24 hours. Reference materials should be prepared as directed by the certificate prior to analysis.

Accessories

528-203 Ceramic Combustion Boats**, 761-929 Crucible Tongs, and 501-614 Spatula

***Note: For optimal precision, ceramic combustion boats should be baked in a muffle furnace at 1000 °C for a minimum of 40 minutes. Once the ceramic combustion boats have cooled, they should be transferred to a desiccator for storage. If the ceramic combustion boats are not used within twenty-four hours, they should be re-baked. After baking, handle ceramic combustion boats with clean tongs only; do not use fingers.*

Reference Materials

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

General Parameters†

Gas Type	Helium or Argon
Furnace Temperature	1350 °C
Ramp Rate	12 °C/min
Dehydration Time	0 s
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	4 s
Dose Loop Size	Large (10 cm^3) or Small (3 cm^3)

Element Parameters†

	Helium (10 cm^3 & 3 cm^3)		*Argon (10 cm^3 & 3 cm^3)*	
	Carbon	*Nitrogen*	*Carbon*	*Nitrogen*
Wait for Baseline Stability	Yes	---	Yes	---
Integration Delay	15 s	0 s	15 s	9 s
Starting Baseline	1 s	10 s	1 s	10 s
Post Baseline Delay	5 s	25 s	5 s	25 s
Use Comparator	No	No	No	No
Integration Time	22 s	50 s	22 s	70 s
Use Endline	No	Yes	No	Yes
Endline Delay	---	30 s	---	30 s
Ending Baseline	---	5 s	---	5 s
Use Profile Blank	---	---	---	Yes

†Refer to 928 Series Operator's Instruction Manual for Parameter definitions.

Burn Profile

Burn Step	*Lance Flow*	*Furnace Flow*	*Time*
1	No	Yes	5 s
2	Yes	Yes	5 s
3	Yes	No	End

Procedure

1. Prepare 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 (ceramic combustion boat is not required).
   b. Initiate the analysis sequence.
3. Determine Blank.
   a. Select five or more Blank replicates in the Login screen.
   b. Place 528-203 Ceramic Combustion Boats in the appropriate positions in the autoloader.
   c. Initiate the analysis sequence.
   d. 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 both elements when utilizing Helium as a carrier gas, and less than or equal to 0.005% (50 ppm) for both 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 of a suitable reference material into a 528-203 Ceramic Combustion Boat.
   c. Enter sample mass and identification into the Login screen.
   d. Transfer the ceramic combustion boat containing the reference material to the appropriate position in the autoloader.
   e. Perform steps 4b through 4d a minimum of five times for each calibration/drift material used.
   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 by analyzing an appropriate mass of another/different suitable reference material and confirm that the results are within the acceptable tolerance range.
5. Analyze Samples.
   a. Select the desired number of sample replicates in the Login screen.
   b. Weigh ~ 0.20 g of a Carbon black or graphite sample into a 528-203 Ceramic Combustion Boat.
   c. Enter sample mass and identification information into the Login screen.
   d. Transfer the ceramic combustion boat containing the sample to the appropriate position in the autoloader.
   e. Perform steps 5b through 5d for each sample to be analyzed.
   f. Initiate the analysis sequence.

TYPICAL RESULTS

Data was generated utilizing a linear, full regression calibration for Carbon determination and a linear, force through origin calibration for Nitrogen determination, using fractional masses (0.17 g to 0.30 g) of LECO 502-642 (Lot 1020) LCRM Phenylalanine (65.45% C, 8.46% N). The calibrations were verified using LECO 502-896 (Lot 1007) LCRM EDTA (41.14% C, 9.59% N). Carbon black samples were dried at ~125 °C for at least one hour prior to analysis in accordance with ASTM D7633. Graphite samples were dried at ~105 °C for one hour prior to analysis. Dried samples were stored in a desiccator until used for analysis (within 24 hours). Samples were weighed and analyzed at ~0.20 grams.

	10 cm³ Helium			**3 cm³ Helium**			**10 cm³ Argon**			**3 cm³ Argon**		
	Mass (g)	*% C*	*% N*	*Mass (g)*	*% C*	*% N*	*Mass (g)*	*% C*	*% N*	*Mass (g)*	*% C*	*% N*
Graphite Powder	0.2094	100.0	††	0.2051	100.0	††	0.2066	100.0	††	0.1990	99.9	††
LECO 502-634	0.2003	100.1	††	0.2050	100.1	††	0.2007	99.9	††	0.2057	99.9	††
Lot 1000	0.1998	100.1	††	0.2021	100.0	††	0.1958	99.9	††	0.1965	100.0	††
100.0% ±0.3% C	0.2042	100.1	††	0.1992	100.0	††	0.2040	99.8	††	0.1975	99.9	††
	0.2080	100.0	††	0.2033	100.0	††	0.1965	99.9	††	0.2055	99.9	††
	Avg =	***100.1***	**--**	***Avg =***	***100.0***	**--**	***Avg =***	***99.9***	**--**	***Avg =***	***99.9***	**--**
	s =	***<0.1***	**--**	***s =***	***<0.1***	**--**	***s =***	***0.1***	**--**	***s =***	***<0.1***	**--**
Carbon Black	0.2054	93.5	0.25	0.2056	93.7	0.22	0.2016	93.9	0.26	0.1995	93.7	0.12
LECO 502-196	0.1992	93.8	0.24	0.2003	93.7	0.22	0.2044	93.9	0.23	0.2093	93.6	0.15
Lot 1711	0.2017	93.8	0.24	0.2024	93.9	0.22	0.2036	93.8	0.27	0.2025	93.6	0.19
	0.2036	93.8	0.24	0.1983	93.5	0.22	0.2045	93.7	0.26	0.2046	93.6	0.20
	0.2047	93.8	0.24	0.2015	93.5	0.23	0.2083	93.7	0.27	0.2024	93.5	0.13
	Avg =	***93.7***	***0.24***	***Avg =***	***93.7***	***0.22***	***Avg =***	***93.8***	***0.26***	***Avg =***	***93.6***	***0.16***
	s =	***0.1***	***<0.01***	***s =***	***0.1***	***<0.01***	***s =***	***0.1***	***0.01***	***s =***	***0.1***	***0.04***

††*Nitrogen values were below the method detection limit.*

LECO Corporation | 3000 Lakeview Avenue | St. Joseph, MI 49085 | Phone: 800-292-6141 | 269-985-5496
info@leco.com • www.leco.com | ISO-9001:2015 Certified | *LECO is a registered trademark of LECO Corporation.*

