

CARBON, HYDROGEN AND NITROGEN BY OXIDATIVE PYROLYSIS

UOP Method 866-86

SCOPE

This method is for simultaneously determining organically based carbon, hydrogen and nitrogen in coals, cokes, oils and other materials. The detection range for each element is 0.04 to 100 mass-%. Water contained in the samples will contribute to the hydrogen values. Solid samples containing greater than 5% sodium carbonate may be incompletely pyrolyzed resulting in low carbon values.

OUTLINE OF METHOD

Two basic types of carbon-hydrogen-nitrogen analyzers are available. These are distinguished by the detection method for the carbon and hydrogen. This method describes a LECO analyzer, however, other instrumentation may also be satisfactory (see *APPENDIX*).

The LECO Carbon-Hydrogen-Nitrogen Analyzer is microprocessor controlled and includes a balance, two-zone furnace and detection system. The detector system consists of two individual infrared (IR) cells for detecting the carbon as CO₂ and hydrogen as H₂O, a thermal conductivity detector for detecting the nitrogen as N₂, a mixing cylinder, an aliquot valve, scrubbers and a hot copper reaction tube.

A sample is weighed into a capsule and combusted in a stream of ultra high purity oxygen. The combustion products are passed through CO₂ and H₂O IR cells to monitor the combustion cycle, and the products are collected in a mixing cylinder. Upon completion of the combustion cycle any additional volume remaining in the mixing cylinder is filled with ultra high purity oxygen. The combustion products are then recycled back through the IR cells, where the CO₂ and H₂O levels are determined. The microprocessor takes the detector outputs and calculates the carbon and hydrogen values, while an aliquot of the combustion products is automatically injected into a stream of helium. The aliquot passes through a hot, reduced copper bed that converts all of the nitrogen compounds to N₂ and removes oxygen. After scrubbing to remove the CO₂ and H₂O, the remaining gases are passed through a thermal conductivity detector and the microprocessor then calculates the mass-% nitrogen concentration. All the calculations are performed relative to a preanalyzed standard, or standards, that is similar in composition to the sample.

APPARATUS

Auto sample drop kit, for Model CHN-600, LECO, Cat. No. 778-470 (optional)

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Carbon, Hydrogen and Nitrogen Analyzer, LECO Model CHN-600, LECO Corp., Cat. No. 785-500, was used in the development of this method. Equivalent instrumentation may be utilized.

Regulator, carbon dioxide, two-stage, Matheson, Model 8L-320, or equivalent

Regulator, helium, two-stage, high purity, Matheson, Model 3104-580, or equivalent

Regulator, nitrogen, two-stage, high purity, Matheson, Model 3104-580, or equivalent

Regulator, oxygen, two-stage, high purity, Matheson, Model 3104-580, or equivalent

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water mean deionized or distilled water.

Absorbent, sample, COM-AID, magnesium oxide, coarse and fine, LECO Corp., Cat. Nos. 501-426 and 501-427, respectively, or equivalent

Anhydron, magnesium perchlorate, LECO Corp., Cat. No. 501-171, or equivalent

Ascarite II, LECO Corp., Cat. No. 183-001, or equivalent

Capsule, copper, LECO Corp., Cat. No. 501-571

Capsule, tin, LECO, Corp., Cat. No. 501-059, or equivalent

Catalyst heater tube, LECO Corp., Cat. No. 780-911, or equivalent

Carbon dioxide, 99.99% minimum purity

Combustion U-tube, LECO Corp., Cat. No. 776-286, or equivalent

Copper turnings, LECO Corp., Cat. No. 501-621

Crucibles, LECO Corp., Cat. No. 529-026, or equivalent

Furnace reagent, LECO Corp., Cat. No. 501-609

Glass wool, LECO Corp., Cat. No. 501-081, or equivalent

Grease, silicon, vacuum, LECO Corp., Cat. No. 501-241, or equivalent

Helium, 99.999% minimum purity

Lance, quartz, LECO Corp., Cat. No. 776-283

Needles, disposable, 18-gauge, 38-mm length and 22-gauge, 25-mm length, Sargent-Welch Scientific, Cat. Nos. S-79402-G and D, or equivalent

Nitrogen, 99.9%, minimum purity, extra dry

O-rings, LECO Corp., Cat. Nos. 761-651, 772-269, 772-520, 774-425, 775-314 and 776-284, (2 of each required)

Oxygen, 99.99% minimum purity

Paper, roll, LECO Corp., Cat. No. 770-764, or equivalent

Quartz wool wadding, LECO Corp., Cat. No. 501-608, or equivalent

Quick disconnect tubes, LECO Corp., Cat. No. 775-601 and 775-880, (2 of each required)

Reagent N-catalyst, LECO Corp., Cat. No. 502-049

Ribbon and spool, LECO Corp., Cat. No. 770-778, or equivalent

Spatula, LECO Corp., Cat. No. 501-614, or equivalent

Standards, calibration, Alpha Resources Inc., coal, No. 2 diesel, kerosine and residual, Cat. Nos. 2778, 330, 327 and 100, respectively, or equivalent

Syringe, disposable, 3-cc, Sargent-Welch Scientific, Cat. No. S-79401-25A, or equivalent

PROCEDURE

Instrument Start-up

Install the analyzer according to the manufacturer's instructions. Allow the instrument to warm-up. The LECO CHN-600 requires a two-hour warm-up time, other analyzers may require different lengths of time as indicated in instruction manuals.

Operating Conditions

Furnace temperatures

Primary	1050 C
Secondary	1000 C
Catalyst heater	760 ± 25 C
Oven chamber	53 ± 1 C

Carrier gas pressure

Oxygen	275 kPa (40 psi)
Helium	275 kPa

Pneumatic gas pressure

Nitrogen	275 kPa
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Dosing gas pressure

Carbon dioxide	275 kPa
Nitrogen	275 kPa

Gas flow, during operation

Helium	400 mL/min
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Nitrogen comparator level

4

Change crucible

after 10 analyses

Change N₂ reagent

after 150 analyses

Change N₂ catalyst

after 1000 analyses

Change furnace reagent

after 1000 analyses

Lance

Closed

Before operating the analyzer, verify that the furnaces are at the specified operating temperatures. Follow the start-up procedure as outlined in the Instruction Manual to ensure that correct results are obtained. The following are typical operating conditions for the LECO CHN-600 Analyzer. Other operating conditions will exist for different analyzers.

All voltage or electronic unit temperature adjustments should be carried out as described in the Instruction Manual.

Oxygen Flows

The LECO CHN analyzers are provided with a microprocessor controlled feature known as Oxygen Profiles. The Oxygen Profiles ensure that the sample is completely combusted in a minimal amount of time by controlling the oxygen flow rate. If a sample combusts rapidly, such as acetanilide or gasoline, a high initial oxygen flow rate is necessary to ensure complete combustion. However, if a sample combusts slowly, such as a coke or some coal samples, a low initial oxygen flow rate followed by a high oxygen flow rate is necessary.

The flow rates are determined empirically for each sample type. The “Applications Section” of the Instruction Manual provides suggested oxygen profiles for a variety of materials and should be used as a guide when analyzing samples. It should be noted that low and erratic results, and the formation of a soot in the extreme case, are indicative of incomplete combustion and a higher oxygen flow rate must be used.

The number and duration of available flow rates are dependent on the particular model of analyzer and are indicated in the Instruction Manual. The procedure for setting oxygen profiles and any additional information on their use can also be found in the Instruction Manual.

Blanks

An instrumental blank for carbon, hydrogen and nitrogen must be determined to compensate for any contamination present in the analytical gases or in the reagents. The blanks must be run every day and are repeated until low and consistent results are obtained, for example, C = 0.00%, H = 0.00% and N = 0.15%. Follow the procedure as outlined in the Instruction Manual to determine the instrumental blanks.

Calibration

Once the instrumental blanks have been determined, the analyzer can be calibrated. Calibrate the analyzer by analyzing a reference standard that is similar in composition to the samples being analyzed as indicated in the Instruction Manual (see also *Sample Analysis*). Calibrate the analyzer for each sample type that is to be analyzed.

Sample Analysis

To ensure reproducible and accurate results, a representative, homogeneous sample must be obtained. Light distillates in the gasoline/kerosine boiling range, which are not viscous, are shaken and sampled. Higher boiling liquids, which are viscous at ambient temperature, are gently heated, shaken and sampled. Solid samples are either ground, if they are hard enough, or sampled as carefully as possible.

Follow the appropriate preparation technique and proceed with the analysis as outlined in the Instruction Manual.

CALCULATIONS

The calculations are performed by a microprocessor, which is directly interfaced to the analyzer.

PRECISION

The precision data were obtained using a LECO CHN-600 Analyzer and are not necessarily applicable to other analyzers.

Based on the number of replicates shown, the estimated standard deviation (esd) for carbon, hydrogen and nitrogen were calculated at the levels shown in the table below. Duplicate results by the same operator should not differ by more than the allowable difference shown (95% probability).

Sample Type	Number of Replicates	Concentration, mass-%	esd, mass-%	Allowable Difference, mass-%
Light Distillates				
C	6	83.41	0.95	3.47
H	6	13.26	0.11	0.40
N	6	0.04	0.04	0.14
Heavy Oils				
C	6	86.27	0.27	0.99
H	6	12.99	0.02	0.09
N	6	0.34	0.07	0.26
Solids				
C	6	27.07	0.15	0.55
H	6	0.88	0.02	0.07
N	6	0.07	0.04	0.14

TIME FOR ANALYSIS

The elapsed time and labor requirement for a single sample run in duplicate is 0.25 hour. The elapsed time for 3 samples in duplicate is 0.75 hour while the labor requirement is 0.33 hour.

REFERENCE

Instruction Manual for LECO Model CHN-600, LECO Corp.

SUGGESTED SUPPLIERS

Alpha Resources Inc., 3090 Johnson Road, Stevensville, MI 49127
 LECO Corporation, 3000 Lakeview Ave., St. Joseph, MI 49085-2396
 Matheson Co., P.O. Box 96, Joliet, IL 60434
 Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077

APPENDIX

Other types of Carbon-Hydrogen-Nitrogen Analyzers, which are typified by the instruments manufactured by Perkin-Elmer Corp., Carlo Erba Strumentazione and W. C. Heraeus GmbH, use only thermal conductivity detectors. The sample is combusted in a high temperature resistance furnace in either a stream of helium, which has been enriched with oxygen, or in an aliquot of pure oxygen. The subsequent combustion products are completely oxidized by a catalyst. The oxygen in the combustion products is then removed and all of the nitrogen is converted to N_2 . Each instrument uses thermal conductivity to quantify the result, but by different techniques.

The Perkin-Elmer uses 3 thermal conductivity detectors. The CO_2 and H_2O are determined sequentially by passing the combustion products through the first detector, scrubbing either the CO_2 or H_2O from the gas and passing the scrubbed gas through the second detector. The N_2 is then determined by passing the scrubbed combustion products through a third thermal conductivity detector.

The Carlo Erba uses a chromatographic column to separate the N_2 , CO_2 and the H_2O . A thermal conductivity detector is used to quantify the peaks.

The Heraeus uses an adsorption-desorption technique to separate N_2 , CO_2 and H_2O . A thermal conductivity detector is used to quantify the peaks.

As with the LECO Analyzers the Perkin-Elmer, the Carlo Erba and the Heraeus use a microprocessor to perform calculations. The analyzers must be calibrated with a standard material that is similar in composition to the samples being analyzed.